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Modern Ideas Concerning the

Direct Dyes and Cellulose

From the Viewpoint of Substantivity

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THIS paper describes briefly the modern views on the absorption of direct dyestuffs by cellulose and their physical properties. Although much work has been done in the past on cellulose and also on the chemical nature of the direct dyestuffs, the system (dyestuff-cellulose) has not been investigated to any great extent. This is rather surprising in view of the great technical importance of the subject but it can be explained on account of the fact that there has been up till recently no accurate method available for estimating small quantities of the dyestuffs. Chemical methods such as those put forward by Trotman[1] cannot easily be applied to really small quantities of the dye so that the method which now seems most useful for absorption measurements is a colorimetric method recently developed. Nothwithstanding the lack of accurate quantitative data on this subject many theories have been put forward to account for the phenomenon called dyeing. The oldest theory supposed the dye particles to enter into the wet fiber via the "pores" and on subsequent rinsing and drying the pores closed and shut in the dyestuff. The dye is held entirely mechanically and so this theory is called the mechanical theory. Because acid dyes were taken up in molecular ratio by wool Knecht and Vignon were of the opinion that a chemical compound was formed and so enunciated the chemical theory[2] to explain dyeing. O. N. Witt[3], however, disagreed with both these theories and imagined a solid solution to be formed.

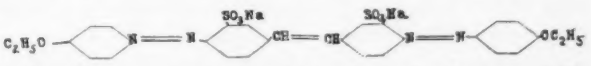
With the discovery of the phenomenon of absorption, Freundlich thought that dyeing must be due to this, because the concentration at the surface was greater than at the center of the adsorbant, but an opposing theory called the colloidal theory, also arose a little later. In this theory it is supposed that the union of dyestuff and cellulose was due to each neutralizing the charge on particles of the other and so causing mutual aggregation, just as two oppositely charged colloids are flocculated when mixed.

None of these theories alone, however, can explain the actual facts. Together they may do so, but separately each one only explains one particular aspect of the dyeing process. The chemical theory is generally accepted for acid and basic dyes on wool but obviously it cannot apply to any other classes of dyes which are not taken up in molecular proportions.

The Dyestuffs

The direct dyestuffs may be classified under five headings according to their chemical constitution.

Firstly there are the dyes derived from diaminostilbene disulfonic acid by tetrazotization and coupling with suitable end components. To this class belongs Chrysophenine G in which the end component is Ethoxy benzene.



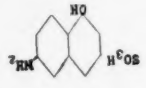
Dyestuffs such as "Sun Yellow" may also be derived from the dinitro compound by mild reduction. The second class of dyes comprises those formed by tetrazotization and subsequent coupling with suitable end components of benzidine and its homologues—dianisidine, toluidine, dichlorbenzidine, etc. These dyes cover a wide range because many end components, phenols—animines—naphthols—napthylamines—are available and one diazo group of the tetrazotized base couples more quickly than the other, enabling two different end components to be coupled.

The classical example of this class is Congo Red. Whereas the stilbene dyes are mostly yellow these cover

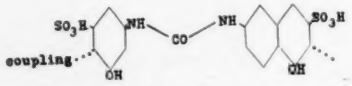
a wide range of reds, blues, yellows, browns; greens however rarely occur.

The dyes formed from toluidine and sulfur are the third class. These use dihydrothitoluidine and primuline as active components.

Dyes derived from J acid can be called the fourth class. J acid itself



may act as an active component as in Fast Red K or it can be condensed with $COCl_2$ to form a urea which also acts as an end component as in Benzo Fast Scarlet 4BS coupling:



The last class of dyes is derived from cyanuric chloride, by condensing it with amines, resulting in elimination of hydrochloric acid, and using this as an active component. To this class belongs Chlorantine Fast Green BL, the exact constitution of which is covered by a patent taken out by the Society of Chemical Industry in Basle[4].

In all cases the actual dyestuffs are sodium salts of complex organic molecules containing sulfonic acid groups. They exist in solution as colloidal electrolytes of varying particle size and are represented as in case of soaps[5] by:— $Na_n R = n\ Na^+ R^-$

The solubility in water varies—although they are all soluble to some extent—those which possess the most SO_3Na groups seem to be most soluble. Many of the dyes are, however, completely insoluble in alcohol, while mixtures of alcohol and water almost invariably form good solvents.

When treated with acid a "dye acid" is liberated and this is usually quite insoluble and very often not the same color as the sodium salt (e.g., Congo Red, which is used as an indicator.)

Freundlich[6] states that they behave as negatively charged colloids in water but in some respects such as conductivity and osmotic pressure they behave as though they were in true solution. Addition of electrolytes causes flocculation, the necessary amount varying according to the nature of the dyestuffs.

The effect of different electrolytes on the absorption was studied by Victoroff[7] who arrived at the conclusion that the absorption increased with the valency of the cation. If this were entirely true it would tend to support the colloidal theory since the "ability to coagulate" of colloidal solutions of the electrolytes lies in this order[8].

The results however are not very reliable since Victoroff did not dye to equilibrium, but chose one constant time at which to work. This is important because it is now known that the absorption increases with the time but not at the same rate when different salts are used.

Auerbach[9] has suggested that the absorption process is largely one of diffusion. The diffusion of a few dyes in aqueous solution has been studied by Robinson and Hartley[10].

For a long time the particle size of dyestuffs has been deduced from the Stokes Einstein equation by measurements of diffusion. Robinson and Hartley state that this is not possible because the equation takes no account of the electrical forces set up. In the diffusion of a colloidal electrolyte the gradient of osmotic pressure is the active force, the two ions, however, have not the same speed of diffusion, consequently the sodium ions moving the faster tend to set up a potential gradient which greatly affects the speed of the R^- ion—in fact it causes the negative ion to diffuse at the same rate as the sodium ion to preserve electrical neutrality of the system. Addition of traces of a foreign electrolyte can at once reduce the rate of diffusion because not only now is it unnecessary for the R^- ion to diffuse at the same speed as the sodium ion to preserve neutrality since the foreign anion can do so in its place, but also the electrolyte tends to give the solution conductivity and destroy the potential gradient formerly set up.

Many other physical properties of Benzopurpurine 4B and its isomer prepared from m-toluidine have been investigated by Robinson and Mills[11] and from this work much can be gained as to the nature of solutions of the direct dyes.

Viscosity measurements, particle size and flocculation experiments, confirm the fact that the dyestuffs exist as colloidal electrolytes in solution at any rate at room temperature. Viscosities are of the order to be expected in an unhydrated (lyophobic) colloid. Contrary to observations by some workers[12] these authors state that no ageing takes place with the pure dyes and hydrolysis is negligible. With regard to the nature of the particles, examination under the ultra-microscope, with a slight addition of common salt without which nothing is visible, shows the patricles to be non-spherical. Finally they conclude by saying that the dye exists as a totally dissociated colloidal electrolyte and that very little sodium is associated in the complex anion.

It has been mentioned above that the molecule of Benzopurpurine 4B was not spherical. If the dimensions of the molecule can be taken as giving any indication as to the shape of the aggregate then the aggregate will most certainly be longer than it is broad.

This is illustrated by Chrysophenine G which crystalizes from aqueous alcohol in long needles and whose aggregates formed by salting out are distinctly "stringy" in nature.

Dyeing and the Structure of Cellulose

On account of its great technical importance cellulose and its properties have been widely investigated so that only the more salient factors can be dealt with here.

The modern conception of cellulose supposes it to consist of long chains of glucose residues linked together by primary valences and these chains attached to one another

laterally by secondary valences, the whole forming a net-work structure[13]. This is borne out because on complete hydrolysis cellulose yields glucose and also fibers have been shown to have greater strength longitudinally than laterally[14].

Howarth has found two hundred glucose residues in one cellulose chain[15] but in all probability this is a minimum and natural cellulose may actually contain many thousands.

This theory was later opposed by Meyer and Mark who after carrying out the X-ray examination[16] of cellulose were of the opinion that it consisted of small crystalline non-swelling aggregates or "bricks" (the "micellar" theory[17]).

Further X-ray examination shows the presence of amorphous matter so possibly a theory comprising the two, where crystallites are dispersed in a long chain structure will explain all the facts[18].

As regards the physical properties of cellulose, moisture is taken up in steadily increasing amounts with increase in the relative humidity of the air[19]. The amount absorbed at any given humidity varies with the type of cellulose, the activated forms taking up more than cotton[20].

Activation may be brought about in several ways.

Swelling agents enter the molecule and free the hydroxy groups by pushing apart the long chains previously attracted to one another by secondary valences.

The mechanism of the action of caustic soda is to form an ionized sodium salt which attracts water by osmosis and swells the structure[21]. On account of the anisotropic nature of the cellulose such a swelling results in shrinkage in length[22].

Schwalbe[23] studied the action of acids on cellulose and concludes that the chains are actually broken, with the result that aldehyde groups are freed and reducing properties arise in cellulose treated in this matter.

Solution may be effected by violent swelling agents but usually cuprammonium or carbon di-sulfide—caustic soda is used, as for example in the manufacture of viscose. Viscose, since in its manufacture it results from violently swollen cellulose, should have enhanced properties with respect to cotton, and this is indeed the case.

It has already been stated that Freundlich thought that the dye was concentrated more at the surface of the cellulose than in the center. Later work has, however, shown this to be incorrect[24].

If the amount of dye taken up is studied with respect to time, other factors such as salt concentration, concentration of the dye, and temperature being constant, it has been observed that the dye is taken up rapidly at first and that finally an equilibrium value is reached. At such a value the dye is uniformly distributed through the cellulose, consequently a tentative theory was put forward in which the dye diffused into the cellulose via the absorbed water (Neale, Loc. cit.)

The kinetics of the process were found to be identical with the theory of diffusion worked out by A. V. Hill[25].

The general diffusion equation:—

$$\frac{ds}{dt} = K\frac{dc}{dx}$$ (Fick's equa.[26])

s = amount of dye at a depth x cms. below surface
t = time
c = concentration

states that the rate of absorption is proportional to the gradient concentration.

The equation of the accumulation of the diffusing substance at any depth becomes according to Hill

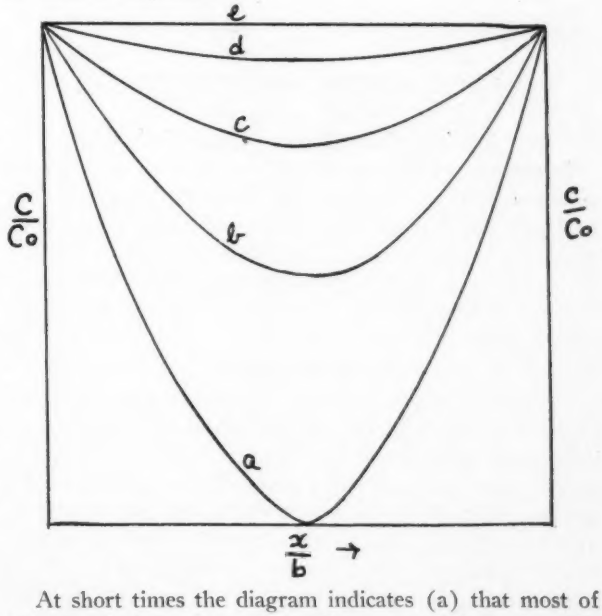
$$\frac{dc}{dt} = K\frac{d^2C}{dx^2}$$

For diffusion into a sheet 2b cms. thick this equation after integration and approximation is:—

$$\frac{C}{Co} = \frac{\text{conc. in absorbent}}{\text{final conc.}} = 1 - \frac{4}{n}e^{-\frac{4Kn^2t}{4b^2}}\ \text{Sin}\ \frac{nx}{2b}$$

By finding values of $\frac{C}{Co}$ and $\frac{x}{b}$ for various times and plotting $\frac{C}{Co}$ against $\frac{x}{b}$ we can get an insight into the nature of the process.

In the diagram the resulting curves are all sine curves of various amplitudes.



At short times the diagram indicates (a) that most of the absorbed dye is at the surface, very little having diffused into the center. With increase in the time (b) the dye is diffusing inwards and the concentration at the center is rising. Finally at infinite time the curve is flat and equilibrium state is reached. No more dye can be absorbed under these conditions so no more can diffuse inward as there is no gradient of concentration and hence no coercive force.

Recent research work indicates that such a process of diffusion of dyestuff into cellulose is a good representation of the kinetics of the process[26].

With regard to the mechanism of the forces, as a result of which the actual absorption of the dyestuff takes place,

no further useful speculations can be made until more quantitative data are available.

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RAYON DYEING AND FINISHING

(Continued from page 658)

Dyeing of Cellulose Acetate Skeins

In general cellulose acetate skeins are dyed in the same manner as are the regenerated cellulose skeins with the exception that dyestuffs suitable for cellulose acetate rayon are used. The methods of handling cellulose acetate skeins are so similar to the method of handling regenerated cellulose skeins that we need not discuss the dyeing of acetate skeins in detail.

Skein Bleaching

Bleached rayon skeins are not sufficiently white to answer the requirements of some manufacturers. This has given rise to a moderate demand for bleached rayon skeins. Also the unbleached rayon skeins that are available on the market are sometimes bought as such and subsequently bleached by manufacturers before further fabric manufacturing operations are carried out.

Due to the desire on the part of skein dyers to produce bleached skeins possessing excellent winding properties and due to the type of equipment available to skein dyers (which is very different from the bleaching equipment used by rayon manufacturers) rayon skeins are often seriously overbleached when the bleaching is carried out after the skeins have been shipped from the rayon manufacturing plant.

Hypochlorite Bleach

The bleaching method most used for bleaching rayon skeins is the well known hypochlorite bleach. The skeins are worked for ten to twenty minutes in a solution containing approximately one and one-quarter per cent available chlorine based on the weight of the yarn treated, after which they are usually given a sour in acid, are rinsed and are considered finished by the bleacher. The use of this procedure has caused a very considerable amount of trouble, as hypochlorite and acid are often left in the fabric. Rayon skeins, after bleaching should *always* be given an anti-chlor treatment with sodium bi-sulfite—the treatment to last at least ten minutes in order that all traces of chlorine shall be effectively removed.

Peroxide Bleach

The procedure given for bleaching tricot and milanese fabric in Chapter VII, "Dyeing and Finishing of Tricot and Milanese Fabrics," can be successfully used for bleaching rayon skeins in the special bleaching apparatus described under the heading of special machines for wet processing skeins appearing in this chapter.

Drying Rayon Skeins

Rayon skeins should be carefully wrapped in a moderately heavy cloth for the extraction operation. It is usual to twist several skeins into a loose "head" or "dole" by giving the skeins one or two twists. Several of these doles—the total approximating 5 lbs.—are then carefully wrapped in a large square of cotton cloth, which has been previously wet out in the liquor from which the skeins have been taken. Unless the skeins are wrapped, as described above prior to extracting, they will be drawn into the small holes of the extractors, which will cut individual filaments and interfere seriously with the winding properties of the finished skeins.

Rayon skeins should not be extracted as thoroughly as are other types of textiles, as a long continued extraction tends to force the yarn lying nearest the outside of the extractor, against the holes of the extractor in such a way that the good winding properties of the skein are reduced. Skeins should be extracted for a few minutes only—that is until sufficient water has been removed to prevent the residual moisture from settling to the bottom of the skein after the skeins are hung on the dryer.

Following the extraction process, the skeins are given a wet finishing operation, the value of which varies with the operator, and the time allowed to handle a given batch. A skilled operator can place the skeins, a few at a time, on a beating pole and can so open up the skein, and adjust the tie bands when necessary, that the winding properties of the dried skein are very materially improved.

After opening the skeins, adjusting the tie bands, beating them out slightly, etc., the skein finisher hangs the skeins on the drying poles.

Regardless of the type of dryer used, the temperature should be kept as low as possible—preferably at or below 140° F. for the best results, although a temperature of 160° F. will not injure the skeins in any way.

Inspection and Sorting for Dark and Light Skeins

It often happens that a particular lot of dyed rayon skeins, through no fault of the dyer, contains some very dark or very light skeins. It is customary to sort each lot of dyed skeins and to segregate off-shade skeins.

(To be concluded in next issue)

Rayon Dyeing and Finishing-16

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Consulting Textile Chemist

CHAPTER VIII—DYEING AND FINISHING OF RAYON SKEINS

(*Continued from page 628, October 23rd issue*)

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DISCUSSION OF GREIGE GOODS

ALL RAYON skeins contain a small amount of oil, soap, or both. They are applied to the yarn to facilitate twisting and winding, to improve the hand, or both.

As many rayon plants are located in hard water regions, and do not have perfectly softened water, small quantities of lime and magnesium soaps are sometimes found present in rayon skeins.

Some skeins are purposely given a scroop finish, which was originally applied to rayon in order to impart to it a "real silk feel," and which is continued at the present time because scrooped skeins possess slightly better winding qualities than do unscrooped skeins.

Before skeins are entered into the dye bath, they should be inspected for the presence or absence of loose ends as too many loose ends will cause tangling during the dyeing operation. When the quantity of loose ends evident appears to be greater than usual, the customer should be notified, and to loose ends tied to the nearest available tie band before the skeins are entered into the dye liquor. This operation requires only a few minutes and aids the subsequent winding operation to such an extent that it is well worthwhile.

The condition of the yarn under the tie band should be carefully observed as it sometimes happens that skeins have been so handled during the wet treating operations within the rayon manufacturing plant, that the tie bands have been moved slightly and have caused tangling of the yarn under and adjacent to said tie bands.

When such a condition is found, it should be noted, one or more skeins withheld from the batch, and the customer notified. It is inevitable that rayon skeins entered in a dye bath with tie bands out of place shall become somewhat tangled during the dyeing operation.

Skeins have a right and wrong side that can be quickly and easily detected. Care should be taken that skeins are always hung on dye sticks in such a way that the inside of the skein comes in direct contact with the stick. Appreciable tangling results when the skein is hung in the reverse position.

DISCUSSION OF SKEIN DYEING EQUIPMENT

Hand Tubs

An appreciable percentage of skein dyed rayon is today still handled under the old hand tub system. When skeins are dyed in this manner, they are hung on sticks and are subsequently immersed in the dye bath suspended from the sticks. The dye tub consists of a wooden, copper or monel tub, usually built two feet deep, two feet wide and from five to forty feet long.

There are two words and two terms used in skein dyeing that need definition for those unacquainted with the art. These terms are, "move" and "turn."

After the skeins are immersed in the dye tub the sticks are moved in pairs in the direction of the length of the tub approximately two feet which move causes the skeins to open somewhat allowing the dye or scouring liquor to circulate through the skeins. When all of the sticks from which the skeins are suspended in a given dye lot, have been moved in this way, the skeins are said to have given a "move." After an even number of moves (usually 4) the skeins are given a "turn."

The term "turn" is used to describe the operation that moves the skeins from their position on individual sticks. In performing the turning operation, the operator grasps the skeins firmly with his thumb and one finger, and raises them a short distance (4 to 8 inches) above the stick and allows them to settle back into the liquor in such a way that the part of the skein projecting out of the liquor before the turn is submerged in the liquor after the turn.

Most dyers figure on giving the skein one turn after each four moves, and have their skein dyeing liquor so constituted that two to five turns will complete the dyeing operation.

Skein Dyeing Machines

The Buhlmann and Smith Drum skein dyeing machines, that gently turn skeins, have replaced the hand tubs in most skein dyeing plants possessing sufficient capital to install the same.

These machines consist of monel metal tubs or tanks, which contain the dye liquor, and large porcelain or glass

movable arms that support and move the skeins throughout the dyeing operation.

The machine is so constituted that the entire lot of skeins can be raised from or lowered into the dye liquor in one operation. Also, skeins are continually worked as long as they are suspended in the dye liquor. The operation of these machines is so simple and gentle that skeins can be worked for a longer period of time on these machines than in hand tubs without serious impairment of winding properties.

Klauder-Weldon Type

The improved Klauder-Weldon type skein dyeing machines have been very successfully used for the processing of rayon skeins. The operation of these machines is so well known throughout the dyeing industry that further discussion here is unnecessary. Dyers using these machines claim results equal to the results produced on the more expensive machines, described above.

Fountain Type

A recent development in the skein dyeing field is a machine that wet processes skeins by flooding them with liquor that sprays up from a pipe on which the dry skeins are originally placed, with sufficient force to actually float the skeins. The liquor runs down the skeins and is recirculated. The skeins are intermittently turned by a special mechanism. This new Smith Drum machine produces dyed skeins that wind very satisfactorily.

Special Machines for Wet Processing Skeins

Many mills have designed, built and installed special machines for the wet treating of rayon skeins, one of which, through the courtesy of Mr. Cromer of the Cromer Brothers Co., will be described in detail here. This machine, which has been particularly successful for skein bleaching rayon skeins, consists of the following parts:—

1. A wooden tub or tank, which contains the dye liquor for the skeins.
2. A false bottom.
3. A false top.
4. A lead pipe liquid circulating system.
5. A closed lead pipe heating system.

Skeins are prepared for bleaching in the above described machine by wetting out for three to five minutes on hand tubs or on the Buhlmann or Smith Drum type of skein dyeing machine, after which these skeins are given one twist into a rough "head" or "dole" and are placed in the machine, that has been previously filled with the bleaching liquor. The skeins are added to the machine in layers, each layer being at right angles to the layer directly beneath. When the machine is filled with the skeins in a loose condition (do not crowd), the false top is put in place and the machine is set in operation. (See bleaching procedure further on for details of bleaching in this machine.)

Wrapping Table

It is customary to provide a table adjacent to the dyeing machines on which the skeins can be wrapped in cloth prior to the extracting operation. The tops of these tables usually consist of a series of slats in order that the dye liquor may drain off freely.

In dye houses operating on the hand tub system, it is customary to use a flat portable "table top" constructed as described above rather than a permanent table.

Straightening Pole

A straightening pole is a large smooth pole projecting horizontally from the wall usually placed three to four feet from the floor. After the extraction, the skeins are placed on this pole for the finishing operation.

Drying Apparatus

Large skein dyeing plants dry rayon skeins in continuous drying systems. The apparatus consists of two long parallel endless belts, which carry the sticks or poles, from which the skeins are suspended, through the drying chamber. The drying chamber contains a heating unit (steam coils), and a fan arrangement that draws air through the heating unit and through the chamber. The most elaborate dryers have a conditioning unit following the drying unit in order that the skeins may immerge from the combined dryer and finisher with their normal regain.

Small skein dyeing plants usually have a room or rooms equipped with a heating unit and a fan. Large racks containing rayon skeins are pushed into these drying rooms where they are allowed to remain until the skeins are thoroughly dried.

Some plants have sufficient space available so that they can allow dyed rayon skeins to dry slowly over night at a temperature not exceeding 100° F. Skeins dried in this manner possess a very pleasing feel and are generally considered to possess better running qualities than skeins dried at higher temperatures.

Skein Scouring

Due to the presence of soap impurities, most skein dyers give skeins a slight wetting out and scouring treatment previous to the dyeing operation.

The scouring bath usually contains 1 to 3% soap or sulfonated castor oil and 1 to 3% of a mild alkaline solution (usually soda ash or tri-sodium phosphate). The temperature is usually 100 to 120° F.; the time of immersion, 3 to 6 minutes.

Following the scouring operation, the skeins are usually raised from the bath and the dye liquor prepared.

Dyeing of Regenerated Cellulose Rayon Skeins

The most important single factor of the rayon skein dyeing process is the time element. In order to be of value, the dyed rayon skeins must be capable of being wound from skein to a spool, cop or bobbin. Lengthy wet processing treatments, particularly at elevated temperatures, can so seriously interfere with the winding properties of dyed rayon skeins, that they are rendered practically worthless. This fact makes time the most important factor in the rayon skein dyeing process, and causes all other factors affecting the process to be so adjusted as to produce the desired results in the shortest possible time.

Whereas it is always desirable to process regenerated cellulose rayon at a high temperature in order to reduce the tendency of rayon skeins to dye different depths in a single dye bath; it is impossible to process rayon skeins at or just below the boil in the machines at present available, as the skeins tend to "open up," or float to the top of the liquor, and become seriously tangled, when processed above 180° F.

It has become customary to enter rayon skeins into a dye liquor, the temperature of which is just above the room temperature, and to give the skeins one turn in this liquor. The skeins are then removed from the dye liquor, the temperature is raised to 130 or 140° F., after which the skeins are set in and given a second turn. Most dyers remove the skeins from the dye liquor a second time, raise the temperature to 160° or higher, and set the skeins in for a third and final move before the first sampling.

The necessity of dyeing skeins in as short a period of time as possible, and at the same time dyeing them at or below 180° F. has caused so much variation from skein to skein within the individual dye lots that the use of skein dyed rayon has decreased constantly during the past three years. Regardless of the pleasing characteristics certain skein dyed fabrics may possess, they are unmarketable or marketable only at a low price, when pronounced warp streaks and filling bars are present.

It is essential that the skeins be worked as gently as possible while in the dye liquor, that they be raised from the dye liquid very slowly and gently, and that they be worked back and forth over the supporting stick or bar in order that the tie band shall not shift too far from its original position during the dyeing operation.

When tie bands are shifted, the winding properties of a finished skein are seriously impaired even though the skein may be given every possible attention in the finishing operation. When tie bands shift, the rayon on one side of the band usually becomes kinky and tangled.

Workmen sometimes tangle skeins during the dyeing operation by grasping the skeins too firmly during the "turning" operation. Skeins should be lifted very gently in order that the yarn does not become matted where handled.

It sometimes becomes necessary to strip and redye skeins due to faulty manipulation, the use of improper dyestuffs, or the failure of the dyer to match the desired shade. Such batches are usually given extremely rapid stripping or bleaching actions in order that the skeins shall be tangled as little as possible during the stripping operation. Often this drastic stripping and bleaching process weakens the skeins seriously and detracts materially from the wearing properties of the ultimate fabric. Stripping and bleaching treatments should be made as gentle as possible, bearing in mind, of course, that treatments cannot be unduly long.

Whereas, it is often possible for the skein dyer to use certain dyestuffs possessing known level dyeing properties (from skein to skein), the requirements of the finished skeins with respect to fastness properties, cost, etc., usually limit the choice of dyestuffs to such an extent that the known level dyeing colors cannot be used.

Although all dye houses have their individual procedures, and these procedures vary slightly one from the other in detail, the following procedure can be considered as representative of the procedures in general use for the dyeing of rayon skeins with direct cotton dyestuffs.

PROCEDURE

Application of Direct Cotton Dyestuffs to Rayon

Per 100 *Pounds of Goods*

(1) Open bundles and place skeins on sticks or on machine
(2) Prepare "wetting out" or scouring liquor containing 1 to 3 lbs. of soap, or 1 to 3 lbs. sulfonated castor oil, and 1 to 3 lbs. of soda ash, trisodium phosphate or other mild alkali.
(3) Work skeins 5 minutes in wetting out bath.
(4) Lift skeins.
(5) Prepare dye liquor at 100° F., adding to the same the necessary dyestuffs plus 3 lbs. sulfonated castor oil.
(6) Enter skeins and work 6 to 10 minutes.
(7) Lift skeins.
(8) Raise temperature of dye bath to 140° F., adding 3 to 5 lbs. Glauber's salt when same is necessary (depending upon dyestuffs used and shades required).
(9) Enter skeins and work 6 to 10 minutes.
(10) Lift skeins.
(11) Raise temperature of dye bath to 170° F. Add Glauber's salt if necessary as explained in No. 8.
(12) Enter skeins and work 6 to 10 minutes.
(13) Lift skeins.
(14) Sample—if necessary continue dyeing process at approximately 170° F. until proper shade is attained.
(15) Remove skeins, wrap in cloth, extract and dry as usual.

Rayon produced by the nitrocellulose process possesses a considerable affinity for the basic dyestuffs without mordanting. This property is taken advantage of when the light bright shades produced by basic dyestuffs are required on rayon.

The procedures used vary considerably according to the shade desired, and the dyestuffs used, the color being applied, in some instances, from a soap bath, and in other instances, from a weak acetic acid bath.

The two following procedures illustrate the two methods of applying basic dyestuffs to nitrocellulose skeins.

PROCEDURE

Basic Dyestuffs on Nitrocellulose Skeins (Alkaline Method)

Per 100 *Pounds of Goods*

(1) Open bundles and place skeins on sticks or on machine.
(2) Prepare "wetting out" or scouring liquor containing 1 to 3 lbs. of soap, or 1 to 3 lbs. lbs of soda

ash, tri-sodium phosphate or other mild alkali.
(3) Work skeins 5 minutes in wetting out bath.
(4) Lift skeins.
(5) Prepare dye liquor at 100° F., dye liquor to contain 1 to 3 lbs. soap, and the necessary basic dyestuff—same to possess the property of dyeing nitrocellulose skeins from a soap bath.
(6) Work skeins 6 to 10 minutes.
(7) Lift skeins.
(8) Raise temperature of bath to 130-140° F.
(9) Enter skeins and work 6 to 10 minutes.
(10) Lift skeins.
(11) Raise temperature of dye bath to 160-170° F.
(12) Enter skeins.
(13) Work 6 to 10 minutes.
(14) Sample—making necessary additions to attain desired shade.
(15) Wrap skeins in cloth, extract and dry as usual.

PROCEDURE

Application of Basic Dyestuffs on Nitrocellulose Rayon (Acid Method)

Per 100 *Pounds of Goods*

(1) Open bundles and place skeins on sticks or on machine.
(2) Prepare wetting-out bath at 120° F., same to contain 2% acetic acid based on the weight of skeins.
(3) Enter skeins and work 5 minutes.
(4) Lift skeins.
(5) Prepare dye bath with necessary dyestuffs and add 1 to 2% acetic acid.
(6) Enter skeins and work 6 to 10 minutes.
(7) Lift skeins.
(8) Raise temperature of dye bath to 130-140° F.
(9) Enter skeins and work 6 to 10 minutes.
(10) Sample—run dyeing until desired shade is attained.
(11) Roll in cloth, extract and dry as usual. (Care must be taken that the cloth used to roll skeins in has been completely wet out in the dye bath. Also, the extracting operation must be as short as possible in order to prevent undue crocking of the dyestuffs during the extracting operation.)

The above described acetic method of applying basic dyestuffs to nitrocellulose skeins is not to be recommended, as it sometimes produces streaks due to the absence of scouring treatment. (The finishing oil used in the skein is not removed.) Another drawback to the use of this process is the fact that the dyestuff is deposited largely on the outside of the fibers and filaments, and can be easily rubbed off even during the extracting and drying processes. That is to say, the skeins dyed in the above described manner "crock" even more than normal basic dyeing. It has been given here simply because it has been successfully used from a commercial viewpoint on a considerable quantity of nitrocellulose process yarn.

The successful application of vat dyestuffs to rayon skeins is very difficult because of the great number of operations that must be carried out and because of the undesirable speed with which these operations must be concluded in order that the finished yarn can be wound with reasonable success. Most vat dyed skeins, that are today used in the production of fabrics, are found to be somewhat uneven within the skein, if carefully inspected, particularly under the tie bands, due to the regrettable speed with which every operation must be pursued.

As a matter of fact, there are few firms who have successfully produced vat dyed skeins capable of being wound and sufficiently level to be used in the manufacture of fabrics.

The following procedure looks and is expensive. However, it has been successfully used in the production of large quantities of vat dyed rayon skeins.

PROCEDURE

Application of Vat Colors to Rayon Skeins

Per 100 *Pounds of Goods*

(1) "Vat" or reduce the dyestuff in the usual manner.
(2) Prepare wetting out bath—
2 lbs. caustic
2 lbs. hydrosulfite
100° F.
(3) Wet out skeins for 5 minutes.
(4) Add caustic and hydrosulfite to wetting-out bath —quantities of each depends on dyestuff used and depth of shade required.
(5) Add 30 lbs. glue.
(6) Raise temperature of dye bath to maximum temperature recommended by dyestuff manufacturer for dyestuff used.
(7) Add one-quarter of "vatted" dyestuff.
(8) Enter skeins and work approximately six minutes.
(9) Lift skeins.
(10) Add one-quarter "vatted" dyestuff.
(11) Enter skeins and work approximately six minutes.
(12) Lift skeins.
(13) Add one-quarter "vatted" dyestuff.
(14) Enter skeins and work approximately six minutes.
(15) Lift skeins.
(16) Add last quarter "vatted" dyestuff.
NOTE: Test reducing power of bath as each dyestuff addition is made. Further additions of hydrosulfite may be necessary.
(17) Enter skeins and work approximately six minutes.
(18) Sample.
(19) When shade is attained wrap skeins as usual and extract.
(20) Hang skeins on dye sticks or rods of machine. Allow to oxidize in the air.
(21) Aftertreat as necessary for dyestuff used.
(22) Extract and dry as usual.

(Turn back to page 654)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

NOVEMBER 6, 1933

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RESUME OF REMARKS MADE BY GORDON D. PRATT AT THE A.A.T.C.C. CONVENTION IN CHICAGO, SEPTEMBER 9th

Mr. Chairman and Gentlemen:

I have the pleasure and privilege tonight of representing Mr. Thorpe Whitaker, the President of the Society of Dyers and Colourists of Great Britain.

Firstly I have to convey Mr. Whitaker's regrets at not being able to be present in person, in response to the kind invitation forwarded by your Association. Secondly on behalf of the Society of Dyers and Colourists we wish the A.A.T.C.C. continued success and prosperity in the future.

I can assure you gentlemen that I too am personally very sorry Mr. Whitaker is not with us tonight for in that case I could be sitting comfortably down below there listening to him rather than be on my feet attempting to convey to you some of his ideas.

Mr. Whitaker, I think, would probably have told you of the early days and formation of the Society, how a few dyers used to meet together periodically to discuss their problems and how this resulted in the formation of the Society of Dyers and Colourists forty-nine years ago. You will see therefore we celebrate our fiftieth anniversary next year and on behalf of the Society I would extend a very hearty welcome to any members of the Association who happen to be in England at that time to come and join in that celebration. I can assure you gentlemen that although perhaps we do not do things on such an elaborate scale as you do, we shall give you a very warm welcome. If you could bring over for that event the very excellent lady trio which we have just had the pleasure of listening to, your welcome may be even more hearty.

The objects and works of our Society are very similar to your own, namely, the advancement of textile and colorist technology in its very widest sense. Our monthly journal is, I think, as highly regarded on this continent for the excellence of its technical publications as it is in Europe. Incidentally I would mention that the journal is a continual drain on the funds of the Society and I think you relieve yourselves of a tremendous responsibility and financial expenditure, when you join as you do in a regular trade publication rather than attempt to publish your own journal.

The publication in 1924 of the Colour Index with a supplement in 1928 marked a notable achievement of our Society and we are proud to say that already over 2,800 copies of that work have been sold in all parts of the world.

Our research work on the Fastness of Dyed and Colored Materials is now practically completed and it is hoped to publish the final report in a few months' time. In this connection we would welcome closer cooperation between the two Societies. Apparently you also undertake a considerable amount of research work and in order to avoid overlapping and to have the adoption of similar

standards it would be, I think, in our mutual interests if we worked more closely together.

I thank you Mr. Chairman and gentlemen for the warm welcome you have given me as the representative of the Society of Dyers and Colourists and personally I would like to express my appreciation of your hospitality. This is my first visit to Chicago and your warm welcome and the making of new friends will always give me pleasant recollections of this city and the A.A.T.C.C.

SUMMER MEETING, SOUTH CENTRAL SECTION

THE summer meeting of the South Central Section of the A.A.T.C.C. was held at the Andrew Johnson Hotel in Knoxville, Tennessee, on the evening of Saturday, September 30th, 1933. Approximately fifty members and guests were present.

At the suggestion of Harold Schroeder, chairman of the Section, Nestor Grotolueschen took charge of the program. He substituted for W. S. McNab who had charge of the arrangements for the meeting. Mr. McNab was prevented by illness from attending; he was sent a telegram expressing the sympathy and good wishes of those present.

Judge "Bob" Williams of Knoxville welcomed the guests on behalf of the city.

A lively program of entertainment was presented during the serving of the dinner.

Malcolm Mackenzie of the Sandoz Chemical Works, Inc., spoke on "Dyehouse Troubles." This was followed by an open general discussion of the subject.

Respectfully submitted,

ANDREW KELLY,
Secretary.

Dyehouse Troubles*

By **MALCOLM MACKENZIE**

Sandoz Chemical Works, Inc., Charlotte, North Carolina

DYEHOUSE troubles are many and varied and my main difficulty is knowing just where to start; some are due to faults in previous processes such as uneven spinning, tight and loose twisting, or uneven tension in the knitting or weaving. As a rule these do not show up until the dyeing has been started and unless the dyer can cover them up he is very likely to be blamed. Of course prolonged boiling, when possible, sometimes helps but as a rule it is almost impossible to get satisfactory results when the goods are not properly made. The dyer in a mill has it much easier than a job dyer for he can trace the fault back to the department that caused it and perhaps have it corrected in future lots.

Mr. Schroeder stated that this paper would deal with raw stock, hosiery and wool. The raw stock dyer, however, has fewer dyeing troubles than any other as he is the first to handle the stock. If his material is properly opened, his machines clean and evenly loaded, and his preparation, such as scouring or wetting-out, thorough, his troubles should be negligible. The only real trouble that the raw stock dyer is apt to have to contend with is lack of equipment, and when he is being rushed he may try to dye a batch in a kettle or piece of equipment that is not suitable. Some time ago a dyer on raw wool was in a hurry and his regular kettle was busy so he tried to dye a camel hair shade by the top chrome method. He forgot that the steam pipe was brass and as a result his lot came out too dull in shade.

Many troubles are caused through false economy in trying to save steam and time, in fact, I believe that more than half of all trouble originates from improper preparation due to these causes.

Recently a concern that was dyeing cotton roving on a package machine complained that they could not get level dyeings on their light shades though they had little or no difficulty with their medium and heavy shades. Due to the shape of the package, which was similar to a bobbin, the circulation had to be run continuously from the outside of the package to the perforated core and the dyeing had not penetrated much over an inch. On investigating it was found that the material had been treated for about ten or fifteen minutes at a temperature of about 180 with a good penetrating agent. Another dyeing was made using only one-half the amount of the same penetrating agent but the goods were boiled for one hour and then the same dyestuff was used. The result was perfect penetration showing simply that the material in the previous lot had not been properly wet-out. On account of the short time

*Presented at the summer meeting, South Central Section, September 30th, 1933.

allowed at a temperature lower than the boil the material had been wet-out only about one inch from the outside of the package. Since only a small quantity of dyestuff was used, naturally it had exhausted itself on the wetted-out material only.

Woolen yarns or pieces that have been properly and thoroughly scoured will dye quite easily if the proper dyestuffs are used. A short time ago a manufacturer of mohair plushes complained that his materials crocked badly and his first thought was that he was using the wrong type of color although his dyer had selected the fastest colors he could get to withstand crocking. Upon investigation it was found that, while his material dyed evenly and withstood every other test, there was a small amount of wool grease left in the goods. Another lot of material was thoroughly scoured by a different process and tested before dyeing to show that the grease had been properly removed, and then the goods were dyed exactly as before, using the same method and formula, and after finishing no crocking was evident. The main trouble had been that they were trying to do the job too quickly and had not taken time or care to prepare the goods properly.

In the dyeing of rayon hosiery a thorough cleansing is necessary to remove the oils that have been used in the manufacture of the rayon. This is essential in order to produce level dyeing. The selection of dyestuffs depends largely upon the type of rayon used, since some rayons have a greater affinity for dyestuff than others. This can be easily controlled by the judicious use of salt and the proper control of temperature so that the cotton and rayon produce a good union.

Selection of proper dyestuff will eliminate many difficulties. The dyer on full fashioned silk hosiery apparently appreciates this more than the average dyer. As a rule he not only selects colors to dye his silk that no more than stain his cotton but also often has cotton colors that will not dye silk. A few do still use cotton colors that will dye both cotton and silk and then use shading colors to tone up the silk but leave the cotton white. Wherever possible all colors used must discharge to a pure white for the style changes vary so that the stock on the shelves today may have to be stripped and redyed an entirely different shade the following week in order to be saleable.

A manufacturer of narrow fabrics on dyeing a tape found that, after drying, the selvedge was slightly darker than the face and when rolled the side was an entirely different shade than the body of the tape, in fact, the difference was so great the customer refused to accept shipment. Several experiments were made using the same dyestuffs. The orange used in the combination had a tendency in drying to run to the sides, so a different combination of colors was used and this trouble was eliminated.

In dyeing cotton skein yarn pastel shades on a bleached bottom, care should be taken in the bleaching. Yarn that has been bleached by the peroxide or the sodium hypochlorite method seems to give little or no trouble, but where the yarn has been bleached in a vat with calcium hypochlorite it is almost impossible to avoid streaks in dyeing. This is probably due to channeling during the circulation of the bleaching liquor and small quantities of calcium being deposited on the goods. In dyeing pastel shades if slow exhausting colors are used and little or no salt the dyeings seem to be more level.

Some time ago there was a demand for a bleached white half hose with a colored celanese clock or stripe. In order to get a good clear white the goods had to be bleached first and then dyed with special colors for celanese afterwards. While these colors are not supposed to dye cotton they will stain to a certain extent and this, of course, spoiled the clear white. Fortunately, many of the colors used for dyeing acetate silk are very fast and will withstand a light bleaching or stripping with hydrosulfite, so the goods were then cleared up by either a light bleach or stripping. Either method produced very good results.

Often in bleaching stockings with a picot edge or anklets with colored yarns in the top, even though the colors are supposed to be bleaching fast, they may at times bleed slightly and have a tendency to stain the white. Usually the white can be cleared satisfactorily with a light strip at about 140 degrees containing a small amount of stabilized titanium sulfate and some sulfonated oil. Care should be taken not to let the bath be too strong or the clearing too long.

In package dyeing the use of refined salt is advantageous as the impurities have been removed and will not filter out on the outside of the package. The difference in cost between coarse mined salt and refined salt may appear quite an item but this cost is saved many times over in the time saved in washing sand and other impurities from the packages.

In dyeing developed colors care has always been taken to prevent strong sunlight from striking the dyeing during the time of diazotizing and developing but the same care should be used when dyeing a vat orange with Golden Orange RRT as this color when in the leuco state is very sensitive to direct sunlight. Arthur E. Weber wrote a very interesting and comprehensive article on this which has been published in the AMERICAN DYESTUFF REPORTER. Care should also be taken in dyeing some of the naphthol reds not to let direct sunlight strike them between the prepare and the developing bath.

To avoid trouble in dyeing it is sometimes necessary to break rules or do what is supposedly wrong. For instance, in dyeing a vat blue with Blue GCD best results are supposed to be obtained by reducing at 120° and dyeing at about the same temperature, but in dyeing rayon skein yarn this method will produce very uneven and streaky dyeing. A good blue that is very level can be produced as follows: start at 100 degrees and run for five

minutes; lift the yarn and raise the temperature to 140 degrees and run another five minutes; lift again and raise the temperature to 200 degrees, add enough hydro to keep the bath in good condition and run for fifteen minutes; lift again and raise temperature again to 200 degrees, bring bath back to condition with sufficient hydrosulfite, run fifteen minutes more, and finish. This method, of course, requires a great deal more hydrosulfite on account of the high temperature breaking down the bath so rapidly. It has been said that dyeing by this method is not as fast as that produced at a lower temperature, but the goods are at least usable and saleable and none of the material has ever been returned and that is the dyer's main worry.

Water is a serious problem in every dyehouse. Most of the water supply in this section is drawn from muddy streams so that it has to be filtered, and care should be taken that no free alum is allowed to pass through to the settling basin. Enough alum should be used to insure a proper floc, and then the proper amount of soda ash used to take care of any free alum. The water when forming a floc should have a pH of about 6.5 or just slightly acid, and then as it goes through the filter beds it should be treated with sufficient soda ash to prevent the water attacking the iron in pipes and boilers. I believe that ideal water for cotton dyeing and bleaching should contain no free alum or iron but be slightly alkaline to prevent rust from forming. Of course, if the water is hard it will be necessary to use a softening system, for without pure water there are bound to be many troubles.

In dyeing goods that are to be vulcanized, care, of course, is used to select colors that are copper and manganese free. It is here that care and cleanliness count in the preparation of the goods, for the allowances on copper, manganese and iron are so small that any carelessness can cause material to be rejected. Grey yarn in some cases may contain as high as .002% of copper, or impure Glauber's salt may contain a small amount. Copper is rarely found, however, in common salt, and for this reason it is safer to use. In dyeing sulfur colors for this class of work it is well to avoid any metal tanks that may have a copper content, regardless of how small, as the risk is too great.

In some mills where a variety of different types of rayon are used, oftentimes a mixup will occur and it is desirable to have a reagent that will quickly determine the types of fiber in the material. Such a reagent has recently been made at Heidelburg, and it is now on the market under the name of Neocarmin W. Neocarmin W is very simple to use and will immediately identify any rayon or other fiber as each different fiber shows up a different color; for instance, cotton shows up a light blue, viscose a wine red, acetate a greenish yellow, cuprammonium a deep full blue.

Some mills do not have sufficient equipment, and the result is poor dyeing due to trying to cut corners and save enough time to get out an extra batch or two. Since the NRA code has been adopted there seems to be a greater tendency to speed up production than ever. If time is to be saved it should be in the loading and unloading of equipment and not in the actual dyeing or preparing time.

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Proceedings of the American Association of Textile Chemists and Colorists

Recent Developments in the Application of the

Fat Alcohol Sulfates*

By **SAMUEL LENHER, Ph.D.**
Technical Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours & Co.

LAST year at the annual meeting of the Association at Greensboro the speaker outlined the general chemical and physical properties of fat alcohol sulfates which are marketed under the names of the Gardinol and Brilliant Avirol products. These new products, which were developed by the H. Th. Boehme A.G. and the Deutsche Hydrierwerke A.G. in Germany, have rapidly established themselves in numerous operations in the textile industry and in many other fields. The du Pont Company has constructed a plant at Deepwater Point, New Jersey, for the manufacturing of the fat alcohol sulfates, and the plant is now producing the Gardinol products.

In textile processing the alcohol sulfates are finding wide use as detergents and penetrants in the preparation and dyeing of all kinds of fibers, and as finishing agents for the finishing of silk, rayon and cotton fabrics. The importance of Gardinol WA, or sulfated technical lauryl alcohol, and of Gardinol CA, or sulfated technical oleyl alcohol, rests primarily on their powerful neutral detergent action. The use of the Brilliant Avirol products, as finishing materials, is based on their pronounced softening properties, on their chemical stability towards ageing, and on the simplicity of their application. The series of fat alcohol sulfates is more resistant to hardness in water than are common soaps and sulfonated oils, they can be used in acid solution, and they are chemically stable when subjected to ageing in bulk or on textile fibers.

Gardinol WA is much more soluble in water than common soaps, and it is consequently a valuable material for aiding in the removal of soaps and alkalis from fibers on rinsing. The Brilliant Avirol products L-142 and L-168, which are prepared by sulfating technical stearyl alcohol, are sparingly soluble in water at room temperature, and possess the property of being retained by fabrics in a semi-permanent finish. Brilliant Avirol L-144, a derivative of sulfated technical oleyl alcohol, is a readily soluble product which combines the high solubility and detergent properties of Gardinol WA with the softening and finishing effects of the other Brilliant Avirols.

The Gardinol products are ideal for the processing of wool, and they have found a definite place as scouring agents and as dyeing assistants for wool. The scouring of wool in the grease with the Gardinol products and soda ash has been carefully studied in both plant and laboratory to establish the scouring characteristics of the two types of Gardinol. It has been demonstrated that Gardinol WA is a superior detergent for scouring limed and pulled wools of a shrinkage up to approximately 25%. The superiority of Gardinol WA on pulled wools lies in the freedom of the scoured wool from lime soaps, and in the ease of control of the scouring bowls during a run. With wool showing a shrinkage of greater than 25%, Gardinol CA is found to be superior to Gardinol WA. Even high grease content wools for worsteds which show a shrinkage of from 55 to 65% or higher are readily scoured with Gardinol CA. These wools, which are the most difficult of all types to scour, are readily scoured in a four or five bowl machine with Gardinol CA and the normal amount of soda ash which is used with the older soap and soda scour (i.e., a solution containing one per cent or less of soda ash). The criterion of the scouring performance in these tests was the amount of residual grease in the scoured wool; wool was considered to be satisfactorily scoured when the residual grease content was less than one per cent of the weight of the original sample. Gardinol CA is the type which is applicable to all grades of wool; Gardinol WA has a marked advantage only for the scouring of pulled wools. A plant run was made in which the regular production of a wool scouring mill was scoured with Gardinol WA and Gardinol CA for a period of weeks. During this run 1,700,000 pounds of wool was scoured with Gardinol WA and Gardinol CA. The run was carried out in such a way that every lot of wool was split in half, and the two halves were scoured under parallel conditions, on separate machines. One-half of the wool was scoured with Gardinol CA Powder and the other

* Presented at Saturday afternoon session, Chicago Convention, September 9th.

half was scoured with Gardinol WA Double Powder. In this run a direct comparison of the efficiency of the two Gardinol types for the scouring of many different types of wool was made. The types of wool scoured during this run included limed and pulled wools, shorn wool, extremely dirty and soiled wools, high grease content wools, fine wools for worsteds, and dry clean wools.

The soda ash consumption for the Gardinol CA scour was one pound of soda ash for eighteen pounds of wool in the grease; and for the Gardinol WA scour the soda ash consumption was one pound of soda ash for seventeen pounds of wool in the grease. The Gardinol CA consumption was one pound of Gardinol CA for 1,200 pounds of wool in the grease over the duration of the entire run; the Gardinol WA consumption was one pound of Gardinol WA for 960 pounds of wool in the grease for the duration of the run.

This test, and many supplementary plant tests showed conclusively that Gardinol CA is the most satisfactory general wool scouring detergent of the fat alcohol sulfate type. Plant runs have shown that control of the scouring trains is easier using Gardinol than when soap is used. This is probably due to the fact that bowls containing Gardinol and soda ash remain in good condition without additions of chemicals for a longer period than those containing the soap and soda ash. Once a mill operator is accustomed to the use of the powerful Gardinol detergent he finds that control of his operation is made markedly easier than with soap. Mill men advise us that this is an outstanding advantage of Gardinol over soap.

A new and improved type of Gardinol CA for wool scouring has been developed in our laboratories. This product, which will shortly be brought on the market, has been found to be the fat alcohol sulfate product which is most efficient for wool scouring. This product has been selected from thirty-four different experimental samples of the Gardinol CA type as being the one which combines good solubility and hard water resistance with powerful detergent properties.

The Gardinol products have not as yet proved entirely satisfactory for the scouring and wet finishing of woolen and worsted piece goods. The reason for this is that solutions of the alcohol sulfates do not possess sufficient body or a sufficiently high viscosity to exert the necessary mechanical action on the goods for the removal of dirt, such as chalk marks and graphite stains. When the Gardinols are used with soap they aid greatly in producing clean goods by preventing the precipitation of lime soaps and by allowing the rinsing time to be greatly reduced. Certain products which contain appreciable amounts of free fatty acids and common soaps, are being marketed at present as hard water resistant textile assistants. The soap-like action of these assistants is due to the viscous soap solutions which are formed, and is not due to the action of the assistant alone. These materials, like the Gardinols, are not entirely satisfactory without the use of soap, but they have the soap or fatty acid incorporated directly in the marketed mixture. It is probable that development work in progress will uncover combinations of the fat alcohol sulfates with other equally stable chemicals which will solve some of the scouring problems which are not solved by the Gardinol products in their present form.

The Gardinol products make a valuable addition to baths for dyeing wool. They assist greatly in maintaining level dyeing, and they are especially useful on hard twist yarns and fabrics. A concentration of two to four ounces per hundred gallons of dye liquor has been found to be valuable. The Gardinol products are being used to replace a part, or in some cases all of the Glauber's salt which is used in dyeing wool with acid dyestuffs. When part of the Glauber's salt is replaced by a small amount of Gardinol the dyed wool is much softer and more open than when Glauber's salt alone is used. The actual amounts of Glauber's salt which can be replaced by small amounts of Gardinol depend on the dyestuffs used and on dyeing conditions, and actual trial must determine new dyeing formulae with Gardinol.

Gardinol CA is being used in the backwashing of tops. Backwashing is carried out with the minimum of felting when soda ash is used alone in the first bowl and Gardinol CA is used in the second bowl, at a concentration of from 6 ozs. to one pound of Gardinol CA per hundred gallons.

The fat alcohol sulfates do not exert any felting action. This is, of course, a great advantage in all wool processing operations with the exception of fulling, but even in fulling the Gardinols have been found to be useful additions to fulling soaps. It has been found that the addition of a small amount of Gardinol to the fulling liquor aids in the penetration of the heavy fulling mixture and effects a shortening of the fulling time. In some instances the fulling time has been cut 25%. Gardinol also aids in the removal of the fulling liquors on rinsing. With some fabrics the addition of Gardinol to the fulling liquors has enabled a 50% reduction to be made in the rinsing time.

Gardinol WA is finding wide use for the washing of heavy felts, such as the felts which are used on a Fourdrinier paper machine. The older method of washing paper mill felts comprised the use of trisodium phosphate or of soap and soda ash. These strongly alkaline materials are difficult to remove from the heavy felt, and in most mills it has been necessary to remove the felt from the paper machine and wash the felts in a special washer. This operation caused the loss of considerable time when the paper mill was in operation, since an hour or more of rinsing was necessary to free the felt from residual alkalis. Felts can be washed directly on the Fourdrinier machine, using one pound of Gardinol WA to fifty gallons of water with a felt of ordinary weight. The rosin size, clay, pitch, inorganic soil, and other dirt which accumulate on the felt is effectively removed by the Gardi-

nol, and after a rinse of from fifteen minutes to one-half hour the felt is found to be in a clean, open condition.

Gardinol WA is also being used for the wetting-out of new felts for paper machines. If eight ounces of Gardinol WA in fifty gallons of water is used for wetting-out the new felt, the felt can be wet-out and rinsed and ready for use in a quarter of an hour.

The resistance of fat alcohol sulfates to salt solutions makes them of great value as scouring agents for printed cotton goods. The Gardinol products act as excellent detergents for scouring prints in salt solutions to prevent running or bleeding of the colored prints. Production of prints can be increased by the use of Gardinol and salt solutions instead of soap and fresh water by effecting a reduction in the number of changes of baths. Excellent color values of vat prints are obtained with Gardinol and salt scour.

The bleaching of wool and cotton to a clear white with hydrogen peroxide is assisted by the addition of a quarter of one per cent of Gardinol WA, based on the weight of the fabric. It has been found that the uniformity of a hydrogen peroxide bleach is appreciably improved by the use of Gardinol as an assistant.

The fat alcohol sulfates are useful in the soaking of silks for throwing. It has been found that Gardinol WA and Gardinol CA and Brilliant Avirol L-144 are excellent emulsifying agents for throwing oils. By the use of these materials suitable emulsions can be prepared at a pH as low as 7. Emulsions prepared with fat alcohol sulfates show a high exhaust of the throwing oil on the silk fibers which is desirable to the commission silk throwster. The fat alcohol sulfates appear to act as penetrating assistants for the emulsion, and they do not act on the sericin to solubilize it and remove it as do strongly alkaline soap emulsions. It is thus possible to obtain a heavy take-up of oil, or emulsion, by the silk and to get a soft silk which is in an excellent condition for throwing. Several mills are at present experimenting with Brilliant Avirol L-144 in soaking emulsions to prepare a direct knitting yarn. It seems possible that a silk yarn can be prepared in a Brilliant Avirol soak which may not require conditioning or preliminary wetting-out before knitting.

The Brilliant Avirols are being used extensively for finishing silk, rayon and cotton fabrics. They are used as softening and brightening agents to give a desirable finish to these fabrics. They are used to replace special finishing oils and sulfonated oils such as Turkey red oil and sulfonated tallow. In many instances the small amount of Avirol used gives an apparent body to the fabric which permits the elimination of some of the starch from the finishing formula. The Brilliant Avirols possess what appears to be almost a substantivity for silk and rayon fabrics, which makes it possible to dye and finish a fabric in a single bath. Sulfonated oils do not show this substantivity or exhaust from the bath on fibers. The ordinary sulfonated oils can only be applied to the fiber satisfactorily in a special finishing operation. Since the Brilliant Avirols are chemically stable, and are resistant to oxidation or ageing, they are satisfactory on the highest quality of fabrics. Goods which are finished with Brilliant Avirols do not develop a rancid odor on storage for long periods of time; and whites in fabrics do not cloud or turn yellow. A characteristic of the Brilliant Avirols is that they are most effective as finishing agents for silk and rayon when they are used in very small amounts; often when large amounts are used a desirable finish cannot be produced. It is to be expected that large amounts of oil or softener used in a finish can be replaced with a small amount of Brilliant Avirol; for example, in back-filling a cotton-rayon mixture fabric the older finish consisted of fifteen pounds of a high grade soap and fifteen pounds of wood oil, these finishing agents were replaced with one and one-quarter pounds of Brilliant Avirol L-168 and a better result was obtained. In many finishing operations the use of the Brilliant Avirol enables calendering to be reduced, or in some cases to be eliminated entirely.

One of the properties of the fat alcohol sulfates which has made them of outstanding interest in the textile industry is their resistance to the formation of insoluble calcium salts. It is well known that calcium soaps are quite insoluble, even at elevated temperatures, and that while the calcium salts of sulfonated oils are more soluble than those of soap, they still are relatively insoluble. The solubility of the calcium salts of the sulfates of the normal primary aliphatic alcohols, having from eight to eighteen carbon atoms in the molecule, has been determined at 25° C. These data are given in the following table:—

TABLE I

Solubilities of Calcium Alcohol Sulfates at 25° C.

Compound	*No. of Carbon Atoms*	*Solubility*
Calcium octyl sulfate	8	Over 40 g. per 100 cc.
Calcium decyl sulfate	10	25-30 g. per 100 cc.
Calcium lauryl sulfate	12	300-400 mg. per liter
Calcium myristyl sulfate	14	30-40 mg. per liter
Calcium cetyl sulfate	16	Below 5 mg. per liter
Calcium stearyl sulfate	18	Below 5 mg. per liter

The figures given in Table I may be taken as figures for the limit of the solubility of the calcium alcohol sulfates. The solubility given in the table represents the highest concentration in which the calcium alcohol sulfate shows no separation whatever on standing for twenty-four hours at constant temperature. The solubility of the calcium alcohol sulfates increases rapidly with the increasing temperature until a temperature is reached at which the concentration can be increased many fold with

complete solution. Data showing the minimum temperature for complete solution of the calcium alcohol sulfates at various concentrations are given in Table II.

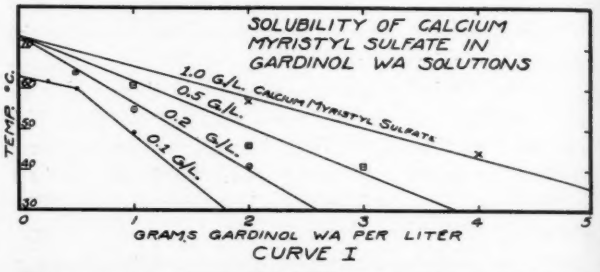
TABLE II

Temperature of Minimum Solubility of Calcium Alcohol Sulfates at Various Concentrations

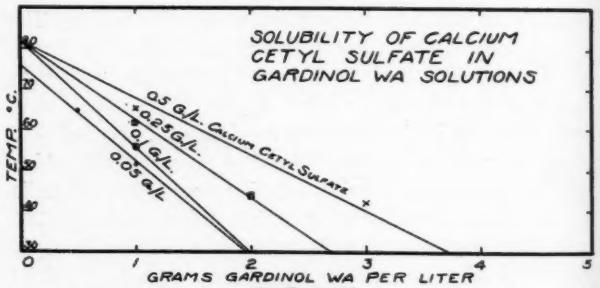
Calcium lauryl sulfate								
Conc. g/l	0.5		1.0		2.0		5.0	
Temp. °C.	53		54		54		54	
Calcium myristyl sulfate								
Conc. g/l	0.05		0.1		0.2	0.5	1.0	
Temp. °C.	58		64		73	73	73	
Calcium cetyl sulfate								
Conc. mg/l	10	20	30	40	50	100	250	500
Temp. °C.	56	65	69	71	76	82	82	82
Calcium stearyl sulfate								
Conc. mg/l		5	10	20	50	100	250	500
Temp. °C.		77	87	93	95	95	95	95

The figures given in Table I and Table II for the solubility of calcium alcohol sulfates cannot properly be used as a criterion of the hard water resistance of the Gardinol and Brilliant Avirol products. The Gardinol and Brilliant Avirol products are sodium salts, and when they are used in hard water they are in a medium in which calcium and sodium ions are in equilibrium with the alcohol sulfate ion. Accordingly the apparent solubility of the salts of Gardinol formed in hard water is that of calcium alcohol sulfates in a solution of sodium alcohol sulfates. It has been found that the calcium alcohol sulfates appear to be quite soluble in solutions of sodium alcohol sulfates. By solubility is meant only apparent solubility, that is, freedom from the formation of precipitates or insoluble salts. It is well known that the Gardinol and Brilliant Avirol products, themselves, are not in true solution in water but, form colloidal sols. Accordingly when it is said that calcium alcohol sulfates are quite soluble in solutions of the sodium alcohol sulfates it is meant that colloidal sols of the calcium salts are formed which show no separation on standing. The apparent solubilities of the calcium alcohol sulfates in solutions of the sodium alcohol sulfates depend upon the concentrations used, the temperature, and the particular salt used.

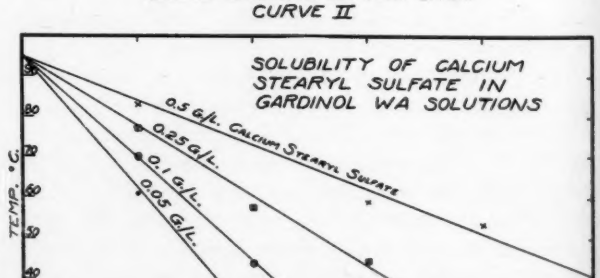
A study has been made of the apparent solubilities of calcium myristyl sulfate, calcium cetyl sulfate, calcium stearyl sulfate, and Gardinol WA solutions over a range of temperatures. The Gardinol WA which was used was a sample of the commercial product, free from inorganic salts, in order to avoid calcium sulfate precipitation. The results of this study of the solubility of these calcium alcohol sulfates and Gardinol WA solutions are given in Curves 1, 2 and 3 of Figure I. It is evident from these curves that as the concentration of Gardinol WA is increased the temperature necessary to secure solution of a calcium alcohol sulfate is lowered. The curves also show that for a given concentration of Gardinol WA the temperature necessary for complete solution is increased as the concentration of the calcium salt is increased. It is interesting to note that small changes of temperature cause very large changes in the solubility of the calcium alcohol sulfates in Gardinol WA solution. The temperature necessary for solution of a given concentration of calcium alcohol sulfate in a given concentration of Gardinol WA increases as the number of carbon atoms in the alcohol sulfate residue is increased. Gardinol CA and the Brilliant Avirol products give similar systems in the presence of calcium salts, and the general conclusions which are drawn from the curves in Figure I can be taken to apply to all the other fat alcohol sulfate products. The magnesium salts of the fat alcohol sulfates are of approximately the same solubility as the sodium salts; consequently the formation of magnesium salts of the fat alcohol sulfates in hard water is never a source of difficulty in their application.



CURVE I



CURVE II



CURVE III

FIG. 1

This brief outline of some of the most important current applications of the fat alcohol sulfates should serve

only as an indication of the many specialized uses which can be made of these new detergents and finishing agents.

Acknowledgment is made to the members of the technical staff of this organization for the developments outlined here. Special acknowledgment is made to Mr. H. L. Jones who carried out the study of the system of the sodium and calcium salts of the fat alcohol sulfates in water.

Discussion

Chairman Cady: Is there discussion of the paper?

Mr. H. G. Smolens: Mr. Chairman, we tried to scour some worsted knitting yarn on sticks using Gardinol and a little soda, in the usual manner. After the yarn was rinsed and extracted and put into a peroxide bleaching solution, it would not sink. We have found that if we try to use Gardinol CA in a peroxide bleaching solution for knitting yarns, the yarn will not sink. I should like to know whether the speaker can explain this fact?

Dr. Lenher: No, we haven't met that difficulty elsewhere and I can't offer you an explanation for it. Gardinol CA type is stable to hydrogen peroxide for a period long enough to cover an ordinary operation, that is, six hours, at room temperature. I don't know how much more stable it is than that.

Is it possible that some slight decomposition of peroxide occurred on the surface of your fiber to form gas bubbles?

Mr. Smolens: There were no bubbles.

Dr. Lenher: They might not be readily visible but they might be there just the same.

Mr. Joseph F. Feit: In our factory we take mixtures of wool and cotton knit goods, and scour them; then after scouring we make up our bleach bath, right in the tank. The goods are not removed from the machine and extracted. They are left right in the tank, in the water, and silicate and Gardinol and bleaching liquor or peroxide are added right to the tank, and we don't have any difficulty with rotation.

Mr. Smolens: We don't have that difficulty where we have circulation, i.e., where the textile is being moved or the solution is being moved.

Chairman Cady: Is there any further discussion, gentlemen?

Mr. Joseph F. Feit: With reference to Gardinol, we have had one peculiar experience in rayon dyeing, that is, dyeing developed blacks.

The dyeing was carried on in the usual manner and then when we reached the stage of diazotizing and developing in our diazotizing bath, using meta toluylene diamine and mineral acid, we noticed we did not get complete reaction. Further, after our developing was completed, wash tests revealed the fact that the dyestuff was not completely diazotized and developed, because the wash fastness was unsatisfactory. It appeared as though the Gardinol had reacted with the meta toluylene diamine in rendering it far more soluble and not permitting it to react in the developing bath which followed later on. We had to discontinue the use of it.

Can you explain that?

Dr. Lenher: Did your dye disappear?

Mr. Feit: No. After we removed the Gardinol we were all right again. We added that purely for lubrication purposes, because the rayon running around in an acid medium has a tendency to sink and cause crease marks in the fabric.

Mr. Harry W. Ericson: Has Gardinol any substantivity either toward the cotton fibers or the cellulose fibers?

Dr. Lenher: The fat alcohol sulfates have no real substantivity in the ordinarily accepted sense of the term for cotton or cellulose fibers. They have a definite substantivity for the wool fiber under acid conditions.

In regard to the preceding question, I should like to ask if the diazotizing bath was tested for acidity in your operation?

Mr. Feit: Well, of course, mineral acids are added right to the diazotizing bath and the operation carried on at a temperature of 55 to 60 degrees, using sulfuric acid.

Dr. Lenher: Was your bath acid at the end of your diazotizing operation with the Gardinol present? Did you test that?

Mr. Feit: We feel quite sure it was because the knit goods were first scoured and then dyed. In the dyeing operation no alkalies are used and as we used soft water, we know the amount of residual alkali present was very small compared to the great amount of sulfuric acid used in the diazotizing operation.

Mr. John J. Sokolinski: I should like to ask the relative softening value, on a cost basis, of Gardinol and a 50 per cent sulfonated tallow, I mean approximately fifty per cent sulfonated oil. I don't know the exact cost of Gardinol—say it is 75 cents a pound. Would that replace, say, a fifty per cent sulfonated tallow at five cents a pound, which would be 15 pounds against one pound, in the handling of your goods in finishing? What is your relative softening value on a cost basis?

Dr. Lenher: The two Gardinol products do not show pronounced softening properties. Those properties are shown by the Brilliant Avirol products. The product which would give you the greatest softening property on fibers in general, that is, cotton fibers or rayon fibers, would be Brilliant Avirol L-168, which contains a certain amount of free technical lauryl alcohol, which is a powerful softening agent. That we have found is an excellent money value and a stable softening agent in comparison with current sulfonated tallows and similar products that are on the market.

Proceedings of the American Association of Textile Chemists and Colorists

Some Uses of Starch Products* in the Textile Industry

By H. A. CROWN

Corn Products Sales Company

THIS subject was originally selected but since, in considering how this paper could be of most benefit to you, it occurred to your speaker that it might be of greater interest to hear about the various starch products, their properties and how to test them. You will no doubt agree that the consumer generally knows more about the uses and applications of his raw materials than the producers of them. Hence it is to the mutual advantage of both consumer and producer for the one to become acquainted with the diverse raw materials and their properties and for the other to learn of the needs and problems of the consumer. For this reason, this paper will touch more lightly on the applications of starches in the textile industry and dwell at greater length on the starch products.

For many years chemists not only in your industry but also in others where starches and their derivatives are used have all asked the same question, namely, "where can I find some good information on starch?" There has been a general desire for more knowledge on this complex subject. "A few things are known but on the whole the structure of starch is still very much of a mystery. This is evident from the fact that the reading of the considerable literature on starch leaves one just about as wise at the end as at the start." This comment was made to me by one of our research chemists who for several years has been working on the structure of starch. Incidentally, I might add that although he has spent several years on it, and he has accumulated considerable information, he feels that there is still more to be learned before the results of his work can be published. However, the more recent book by Walton—a comprehensive survey of starch chemistry—contains some of the best articles on the subject.

Suffice it to say that starch is a complex polysaccharide, the formula being represented as $(C_6H_{10}O_5)n$. The granules consist of an outer membrane or layer now generally called amylopectin and amylose which together with some amylopectin forms the bulk of the inside substance.

Starch is quite prevalent in the vegetable kingdom but the starches of commerce are comparatively few in number, the principal ones being:

Cereal Starches: Corn, Wheat, Rice.

Root Starches: Potato, Tapioca, Arrowroot.

And Sago, which must be classified separately as it is extracted from the "pith" of the Sago palm, grown only in the East Indies.

(I have some microphotographs of various starches, and I will pass them around. You have no doubt seen similar ones before but I will pass them around because these are exceptionally good, clear photographs.)

The process of manufacture in each case is basically one of separation and the starch obtained is what we term thick boiling starch, and as formed by nature, it yields pastes of the highest viscosity. Only when cooked with alkalies, is the viscosity greater than in the original starch. In this respect, all starches are alike, as well as in their chemical composition, as represented by the formula given above. They differ, however, in the size and shape of the granules and in the physical characteristics of their pastes. Corn, wheat and rice starches make a milky white paste with comparatively little stringiness, or as generally expressed, are "short." The root starches, and sago, make a clear paste, with a very definite tendency towards stringiness.

Although they differ in their physical properties, all starches react similarly when treated with acids and subjected to heat. Root starches, however, are more sensitive to this treatment than cereal starches, the reactions take place more rapidly and hence they do not yield as many and varied conversion products as the cereal starches. The reaction is one of hydrolysis and the changes that take place in cornstarch can be considered as representative of this type of reaction.

The following diagram, while not a scientific graph, will graphically illustrate the changes. (Figure 1.)

You might liken the starches separated from the cereal to a car at the top of a hill which has three alternative routes. This is the thick boiling starch (indicating). Route one is an acid treatment in a wet suspension. The starch

* Presented at Saturday afternoon session, Chicago Convention, September 9th.

is suspended in water treated with acid and heat. The first group of products are the thin boiling starches; depending on the amount of acid, the time, and temperature, various modifications are made, getting 20 fluidity, 40, 60, 75, and 90.

The next group of products are the dextrines. Although

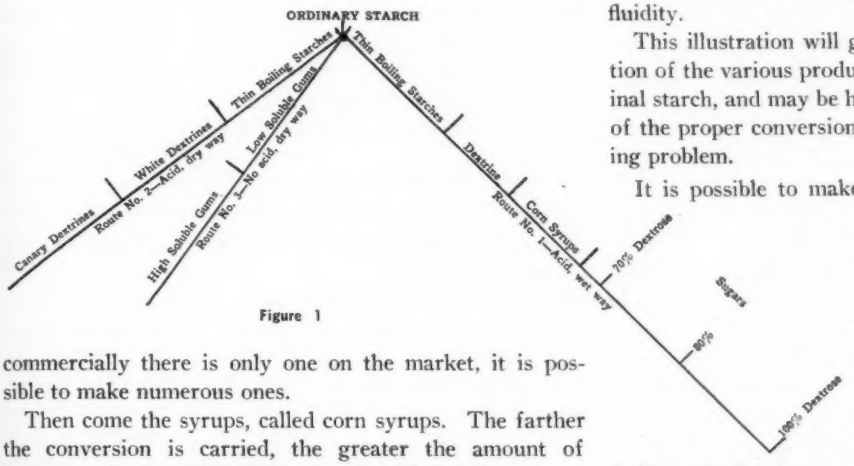


Figure 1

commercially there is only one on the market, it is possible to make numerous ones.

Then come the syrups, called corn syrups. The farther the conversion is carried, the greater the amount of dextrose, the less the soluble starch and dextrine.

Then come the sugars of varying purity. By "purity" we mean the percentage of dextrose, and on the dry basis, commercial products are 70, 80 and 90 per cent.

Finally we have a crystalline sugar which is all dextrose, practically 100 per cent dextrose.

Route 2 is the acid process, but dry. It is a roasting process by which dextrines are made.

I might say, before leaving the other, that products can be made at any point along this line (indicating); the car can be stopped at any point by applying the brakes. There is just a little difference, however, in the procedure in making the conversions, but basically the process or the principle is the same.

By the dry acid method, the first group that can be made are thin boiling starches, but commercially they are not produced in this way. Then comes a range of white dextrines. The nearer the start, the lower the solubility and the fluidity, but the farther you come down on the line, the greater the solubility in cold water, (when we speak of "solubility" we usually refer to cold water, because they are all soluble in hot water) and the greater the fluidity.

Then come a group of Canary Dextrines, and there also the farther you come down the line the greater the solubility and the fluidity.

You notice this line doesn't go any farther, because the conversion cannot be carried on to completeness, because it is a dry roast and there is no further hydrolysis; that is, complete hydrolysis does not take place.

Route 3 is a dry roast, no acid. This is the process used in making British gums, and the range is less because the catalytic agent in this case is the organic acid formed in the roasting. It is similar to making toast, the heat converting the starch. So there isn't as great a range. However, British gums can be made ranging from low soluble and low fluidity at the upper part of the line down to gums as high as 95% soluble in cold water and with high fluidity.

This illustration will give you a visual idea of the relation of the various products to one another and to the original starch, and may be helpful to you in selecting products of the proper conversion when confronted with a new sizing problem.

It is possible to make products which could be represented at every point along any of the three lines. So that if you are using certain starch products now and a new need arises, other conversion products can be made to meet the new requirements.

Many of these products are used in the textile industry. For warp sizing, both thick and thin boiling starches are used, in finishing thick and thin boiling starches, dextrine, corn syrup and sugar, in back filling, thick boiling starch and in printing, starch and British gum are used.

A starch suspension when heated to a certain temperature forms a paste. This transformation takes place rather suddenly and at different temperatures with different starches.

The pasting temperature for corn starch is 160-170° F. and represents the temperature at which the amylopectin begins to absorb water rapidly. The water absorption causes the starch granules to swell to many times their original size. If the heating is continued, the swelling is increased until a number of granules burst open, discharging their content of amylose, which is dissolved in the water, and of amylopectin, which remains suspended in the water in the form of shapeless slimy masses. The result is a more or less viscous paste.

I have some photographs here showing starch both before and after gelatinization. I want you to try to keep in your minds the relative sizes of the granules especially on picture Number 3 after they have been heated to 180 degrees Fahrenheit, because I have some others here I want you to see and to compare them mentally.

It is a very important fact that the viscosity of starch paste is due essentially to the amylopectin and only to a very small extent to the dissolved amylose. In other words, a starch paste is mainly a suspension of particles of amylopectin. A starch paste is occasionally spoken of as a colloidal solution and this is true as far as the amylose is concerned but, as said above, the latter has very little to do

with the properties and the behavior of the paste. It is the size and perhaps to some extent the shape of the amylopectin particles which determine the degree of viscosity.

A starch paste is thickest at the beginning of the boiling because there are still a number of granules left whole in a greatly swelled state and occupying a large bulk. As the boiling continues, more and more of the granules are ruptured and the "sacs" of amylopectin are gradually disintegrated into smaller pieces which occupy less bulk. As a consequence the paste becomes thinner. Agitation by mechanical means helps to make the paste thinner as it aids in breaking up the sticky aggregates of amylopectin which are apt to enclose granules not yet ruptured and thus generally serves to reduce the amylopectin residue into smaller particles. This change takes place more rapidly after the pastes have been cooled down.

The thin boiling starches are starches in which the chemical and the physical characters of the amylopectin have been more or less profoundly modified. The amylose is probably involved to some extent in the change, especially in the high fluidity starches. It can be readily seen, after what was said above about the ordinary starch, that a change in the character of the amylose is of minor practical importance.

I have some pictures here of thin boiling starches which have been gelatinized and you see they have not swelled to the same degree that the thick boiling starches have. They seem to crack open, and upon long heating they break up into smaller particles.

The physical change in the amylopectin, so far as we can observe, consists in a loss in the power of absorbing water, that is to say, in a reduction in the tendency to swelling upon treatment with hot water. The degree of reduction, of course, depends upon the intensity of the chemical treatment of the starch. The difference in the behavior of a 90 fluidity starch upon heating with water, compared to that of a normal starch, is quite striking when observed under the microscope. The granules of the 90F. starch, instead of swelling up balloon-like, increase moderately or not at all in volume but break open in a peculiar manner so that the granules often have an appearance which reminds one of a baked potato broken open. The chemical treatment of the starch has changed the properties of the amylopectin; there is much less indication of swelling and, instead, an evidence of brittleness. It still becomes sticky, however, and the granules show a strong tendency to adhere to each other. These changes are found to a lesser extent, of course, in the starches of lower fluidity and the picture of these starches under the microscope is therefore not so striking as that of the 90 fluidity.

Examination under the microscope of thin boiling starch pastes reveals that starch is made up of concentric layers which flake off the granules. Apparently, therefore, the amylopectin and amylose are distributed throughout the granule, and the indication is that the physical composition of a starch granule is very far from being just the simple one of a shell of amylopectin filled with amylose. There are also evidences that there are subdivisions of microscopic bodies arranged radially in the granule.

Therefore the starches which we call thin boiling when pasted up swell less than ordinary starches and that is why they produce pastes of a higher fluidity or thinness. Another result of the lessened bulk of the amylopectin is that much more starch can be pasted in a given volume than is possible with ordinary thick boiling starch.

When an ordinary or thick boiling starch is examined after pasting, one does not see any or little of the actual structure but in a thin boiling starch the components of the granules have lost their power of swelling, becoming more brittle, the granules break open, and the structure becomes more visible.

The problem of the starch manufacturer has been to devise methods for testing and grading his products for the many industries where they are used, which would establish standards that would conform to the requirements of the consumer.

For many years, a chemical analysis of starch, including acidity or pH value, protein, ash, moisture, fat and fiber determinations had been used as a criterion of quality.

These figures are a check on certain processes in the manufacture of starch but are no indication of how the starch would work in the consumer's plant.

We have expended much time and effort on the determination of viscosity and fluidity of starches. All types of viscosimeters were tried but each of them had some drawback. Extensive work was then done with the Bingham-Green plastometer because with it concentrated starch pastes could be used whereas with the various viscosimeters dilute pastes at high temperatures must be employed. Since in practice, generally a concentration of one pound starch per gallon of finished paste is used, (and these are not viscous but plastic at ordinary temperatures) it was expected that the plastometer would be the means of testing these pastes.

But it too had its limitations, and while still in use for special investigations, our general viscosity determinations are made with the Scott viscosimeter.

Thin boiling starches are classified according to their fluidity. The viscosimeter consists of a glass funnel with the stem cut off at a given length and a glass tip connected with a piece of rubber tubing. This manner of connecting the tip was to facilitate the cleaning when used for a heavy paste. No provision for temperature control in the instrument itself has been made as the paste is tested as soon as transferred, the funnel having just previously been rinsed in water of the desired temperature. The instruments are first regulated so that they will deliver 105 cc. of water in 70 seconds starting with 125 cc. at 25° C. This determination of the water value is only a preliminary

step, the actual standardization being carried out by the use of starches giving pastes of varying consistencies, which consistency has been accurately determined with a funnel and tip which is preserved as a "master instrument" and by which all other instruments are controlled.

In general, the dextrose content of British gums is nil or very low but that of dextrines runs higher.

The important properties governing the workability of dextrines and gums are the soluble content and the paste fluidity. In general, the higher the soluble, the greater the fluidity and the more the sizing solution will penetrate into the yarn or fabric. Hence also the greater the flexibility of the finished goods.

So also with the starches, the higher the fluidity of a starch, the more the size will penetrate while the thicker boiling starches tend to lie on the surface or coat the yarn, producing more stiffness.

For this reason, the modified corn starches can be used to replace the ordinary or thick boiling root starches when market prices make it necessary to effect an economy.

I trust this brief outline of the properties of starches may help you to have a better conception of starches and their derivatives. (Applause)

TESTS FOR STARCH

Starch Fluidity—Scott Viscosimeter

Apparatus:—

Scott Viscosimeter—If necessary enlarge orifice so that the type of starch used will give a good steady flowing paste.

Water bath—Size of bath and method of heating should be standardized as a change in apparatus will effect results. We use a rounded bottom copper water bath 4" deep, 8" in diameter, cover has 3½" opening for copper beaker.

Copper Beaker—Starch is boiled in a beaker 4¾" high tapered from 4" top to 3" bottom.

Method:—

Determinations are referred to a paste made from 15 grams of 12% moisture starch mixed with 280 cc. of water, which is equivalent to 13.2 grams of dry substance starch mixed with 281.8 cc. water. This is a starch concentration of 4.47%.

Procedure:—

Weigh the equivalent of 13.2 grams D.S. Starch into the copper beaker. Calculate moisture in weighed starch. Add 281.8 cc. of distilled water less the amount of water remaining in the starch as moisture.

Example

Starch Moisture	= 10.0%
Grams equivalent to 13.2 D.S.	= 14.666
14.666 — 13.2	= 1.466 grams moisture
281.8 cc. — 1.5 cc	=280.3 cc. water to be added

Stir mixture until starch is completely in suspension and having previously heated the water in the copper bath to boiling place the beaker in the boiling water in the boiler noting exact time. Stir at rate of 110 to 120 r.p.m. for 5 minutes. Regulate flame under the boiler so that the water bath resumes boiling in from 1½ to 2 minutes after beaker is placed in the bath of boiling water. Cease stirring at the end of 5 minutes, place cover on paste-cup and allow to remain in boiling bath for 5 minutes. At this time (10 minutes from the start) stir briskly for about 5 seconds. Allow to remain in the boiling bath for 5 minutes longer. Now (15 mins. from the start) stir briskly for about 5 seconds, remove paste-cup from the boiler and pour 200 cc. of the paste into a marked Erlenmeyer flask which has been kept hot in the water cup of the Scott apparatus which is kept at the boiling point. Immediately transfer the 200 cc. into the Scott funnel. With a stop-watch determine the time required to run out 50 cc. This time in seconds is the result recorded as degrees of Scott fluidity.

Fluidity of Thin Boiling Starch

Weigh 5 grams of starch in a 250 cc. beaker. Add 10 cc. distilled water at 25° C. Stir well to break up all lumps, and make a good smooth cream. Then add 90 cc. of 1% NaOH solution at 25° C. Stir for three minutes at 200 R.P.M. Then place in water bath held at 25° C. for exactly half an hour. The time and temperature are very important in this determination. At the end of the half hour treatment in the water bath pour into a C.P.R. glass fluidity funnel and allow enough starch to run through to fill the tip and note particularly that air bubbles do not remain in tip. Be sure to have all the starch liquor in the funnel to get correct head by returning to funnel the starch which runs through while filling the tip. Using a stop watch quickly place a 50 or 100 cc. graduated cylinder under tip and allow to fill for exactly 70 seconds, and remove quickly or stop flow from funnel. The number of cc. of starch collected in the cylinder in 70 seconds is called the fluidity.

Soluble in Dextrine

Take two grams of the sample in a 150 cc. beaker and stir up with about 50 cc. of distilled water until all is dissolved or is in suspension. It is then transferred to a 200 cc. volumetric flask with 50 cc. more water and allowed to stand for one hour with occasional stirring at room temperature (25° C.) and diluted to the mark with water of 25° C. temperature. The flask is then thoroughly shaken and 100 cc. filtered through a No. 602 S. & S. filter paper, evaporated in a weighed dish and the weight represents the soluble on wet basis.

Dextrine and Gum Fluidity

C. P. R., Tip and Funnel — This consists of a 4 inch funnel and a glass tube drawn to a capillary point. Stem of the funnel is cut square and the capillary tip joined on by means of a short piece of heavy rubber tubing so that it is approximately 5 inches from the apex of

the funnel to the top of the tip. A glass rod covered with a small piece of rubber tubing is used as a plug to tightly close the outlet of the funnel. The funnel is standardized against a master funnel and a graph made showing the variations of the new funnel in comparison with the master.

Procedure

Weigh the correct amount of Dextrine into a porcelain or copper cup (Coors beaker, without lip, 2½" dia., 4½" height). Add the necessary amount of cold water and mix thoroughly. Place on a steam bath for ½ hour, stirring every 10 minutes. Then put in a constant temperature bath held at 77° F. (bath should be large enough that it will not take more than one hour to cool to 77°). Strain through a coarse cloth and run through the C.P.R., tip hold the dextrine paste at as near 77° F., as possible. The number of c.c. flowing through the tip in 70 seconds is recorded as the fluidity. In case funnel has been checked against a standard, it is necessary to correct the reading by consulting the graph.

Discussion

Chairman Cady: Is there any discussion of this paper?

Dr. B. H. Harvey: May I ask a question?

When caustic soda is mixed under proper conditions we get what is known as vegetable blue. Have you any theory as to why cornstarch cannot substitute and take the place of the cassava?

Mr. Crown: That is due to the physical properties only. Cornstarch when mixed with caustic soda will make as strong an adhesive, and could be used for veneer work. In fact, in some instances it is used on so-called cheaper plywood, box shooks, and drawer bottoms, where the degree of adhesiveness or the quality of the work isn't of much consequence. But for table tops and desk tops, and things of that kind, it is not suitable as it requires too much water to put cornstarch into the fluid condition, so it can be applied in the glue spreading machine. As I mentioned at the start, the various starches have different physical properties and so tapioca, which is generally used as a veneer glue, has a cohesiveness and a flow to it which permits its use in the glue spreading machine, and also makes it flow more readily from the glue cooker down to the spreader. Cornstarch would require considerably more water and hence cannot be used for the higher grades of goods.

Does that answer your question?

Dr. Harvey: You are stating a set of conditions but not telling me why. (Laughter)

Mr. Crown: That is something nobody knows. We are trying to find the answer. We are still working on it and some day when our Dr. Sjostrom publishes the results of his researches, we hope we will have the answer for you.

Chairman Cady: Is there further discussion?

Gentlemen, before we adjourn I have one announcement to make.

As most of you know, this is not the annual meeting of this Association in the constitutional sense. Our annual meeting at which officers will be elected will be held in December. The Council voted to hold the annual meeting this year in New York City on December 8th. The meeting will probably be a simple business meeting, held in conjunction with the meeting of the New York Section, and will be the one opportunity for any member who has a grievance to air it in public.

I should like to add that the next annual meeting of the Association will also be held in New York City during the first week of December.

I want to take this opportunity on behalf of the Association to thank all those speakers who have taken part in the technical program, both yesterday and today, and who by their cooperation have made this convention possible.

The meeting will now adjourn. The dinner will be held at seven o'clock and I hope you will all be as prompt as possible.

. . . The meeting thereupon adjourned at five-thirty o'clock . . .

NINETIETH COUNCIL MEETING

(Continued from page 674)

Junior

Malick, Albert—82 School St., New Bedford, Mass. In dyehouse, American Printing Co., Fall River, Mass.

Student

Uzunoff, Boris—Student, N. C. State College, Raleigh, N. C.

Associate

Craft, Lemuel W.—349 Auburndale Ave., Auburndale, Mass. Salesman and Office Manager, E. I. du Pont de Nemours & Co., Inc., 140 Federal St., Boston, Mass.

It was voted that all payments of dues shall be in U. S. currency.

It was moved and voted that the President be authorized to send a letter regarding Sustaining Memberships to each member and a special letter to each of the local Chairmen; these letters to be mailed Nov. 1, 1933.

Mr. Herrmann, representing the New York Section, invited the Association to hold the 1934 Annual Meeting in New York City.

It was voted the Annual Election of Officers for next year be held in New York, N. Y., on December 8, 1933.

A previous motion covering prizes was amended to read—Awards to be announced at Annual Meeting covering period from Nov. 1, 1931, to Sept. 1, 1933.

The meeting adjourned at 3:00 P. M.

Respectfully submitted, A. NEWTON GRAVES, *Secretary*

Proceedings of the American Association of Textile Chemists and Colorists

UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary any vacancies which may occur in their businesses.—A. Newton Graves, Secretary, care Franklin Process Company, Providence, R. I.

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive

NOTE. Persons who have obtained employment should notify the secretary at once. Prospective employers may file vacancies either with the secretary or the AMERICAN DYESTUFF REPORTER.

A-2

Education—B.T.C., Lowell Textile Institute, 1932; also course in shorthand and typing.

Experience—None to date, interested in quantitative analysis, experimental dyeing, color matching, dye testing and dye identification. Ability to learn quickly and will go anywhere. 23 years old, single.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

A-E-2

Education—B.T.C., Lowell Textile Institute, 1933.

Experience—Assistant instructor in chemistry, Lowell Textile Institute. Member of scholastic honorary fraternity.

A-B-C-1

Education—Graduate Industrial Chemical Engineer, Pratt Institute—1911.

Experience—One year as plant control chemist, 4 years as laboratory chemist with gas company, 13 years as plant chemist with bleaching, dyeing and finishing plant. (Rayon and cotton piece goods). Formulated processes and put them into plant operation, 1 year as chemist and demonstrator for dyestuff company, 1 year as superintendent colorist with print works printing linen and rayon, 1 year as director of testing laboratory for national dry goods concern.

A-B-E-1

Education—B.S. in chemistry at C.C.N.Y. Working now on M.A. at Columbia.

Experience—7 years as dye tester and color matcher for dye manufacturer; 6 months skein silk and rayon dyer; 4 years textile chemist and dyer for cotton finishing concern; 2 months boss bleacher and 4 years as teacher of organic chemistry and dyeing. Age 38, single.

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

B-1

Education—Educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following; celanese, rayon, cotton lacks, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-6

Education—Graduate R. I. School of Design.

Experience—5 years in bleachery, 7½ years as assistant dyer, 2 years as boss dyer and 3 years as superintendent of dyeing and finishing. Married, 33 years old. References.

B-7

Experience—4 years as assistant to manager in ribbon mill; 2 years as boss dyer on veils, chiffons and silk skeins; 5 years as boss dyer on ribbons and skeins (cotton and silk); 7 years as boss dyer on spun silk (pure dye and fast) resisted colors; last 12 years as hosiery dyer on silk and cotton, silk-cotton, rayon or wool. 50 years old, married. References.

B-8

Education—Chemistry and Dyeing Department, Philadelphia Textile School.

Experience—Eleven years experience as chemist and boss dyer on the following: woolen, worsted and cotton yarn; woolen, worsted and union piece dyes on both ladies and men's wear; wool, cotton, shoddy and mohair raw stock. Age 33, married, will go anywhere. References.

B-9

Experience—Hosiery dyer with fifteen years' experience on high grade silk hosiery; familiar with all types of machines. Age 43, married. Will go anywhere. References furnished.

B-10

Experience—Ten years in top dyeing for fancy men's wear trade, knitting trade and sports wear; also piece dyeings on men's wear, crepes, sports flannels and tropical suitings; also several years association with commission dyeing trade doing tops, worsted skeins, cotton skeins, piece dyes, peroxide bleaching, naphthols, mohair plushes and imitation caracul cloths. Familiar with many types of machines. 38 years old, single with dependents. References.

F-1

Education—Textile Institute, Alexander Hamilton Inst., Extension work at Brown Univ., working knowledge of German.

Experience—Has had executive departmental work with all types of textiles manufacturers. Acquainted with all types of textile machinery, dyestuff application, laboratory practice, cost methods, and checking methods and processes. References.

NINETIETH COUNCIL MEETING

Sept. 8, 1933

THE Ninetieth Council Meeting of the American Association of Textile Chemists and Colorists was held at the Congress Hotel, Chicago, Ill., September 8, 1933, at 1:30 P. M.

The following were present: Vice-President, Wm. H. Cady; Councilors-at-large, Carl Z. Draves, Walter M. Scott; Councilors, Roland E. Derby, Henry F. Herrmann, representing N. Y. Section; Councilor ex-officio, L. A. Olney, Chairman, Research Committee; Secretary, A. Newton Graves.

The Secretary's balance sheet was read as follows and approved:

Secretary's Balance Sheet—Sept. 8, 1933

Cash on hand June 22, 1933			$301.82
Receipts June 22, to Sept. 8, Inclusive			
Applications	11 @	$5.00	55.00
Applications	1 @	2.50	2.50
Dues (1923)	8 @	5.00	40.00
Dues (Arrears)	2 @	2.50	5.00
Analytical Methods	2 @	.75	1.50
Lightfastness Report,	1 @	1.25	1.25
Reporters			2.50
Royalty on Launderometers			66.00
Worsted Tubing @ postage			10.15
Worsted Tubing, 25 yards, @ .20 per yard			$ 5.00
Yearbooks	8 @	3.00	24.00
Yearbooks	1 @	2.00	2.00
			$516.72
Disbursements			
To Treasurer, Sept. 1, General Fund			217.75
To Treasurer, Sept. 1, Research Fund			82.25
Government tax on checks			.02
Cash on hand, National Bank of Commerce & Trust Co.			216.70
			$516.72

The Treasurer's Report was read as follows and approved:

Treasurer's Report—August 31, 1933

GENERAL FUND

Cash on hand, June 23, 1933	$7,516.91
Receipts, June 23, 1933, to August 31, 1933	3.28
	$7,520.19
Expenditures, June 23, 1933, to August 31, 1933	255.15
Balance	$7,265.04

RESEARCH FUND

Cash on hand, June 23, 1933	$1,459.14
Receipts, June 23, 1933, to August 31, 1933	2,150.00
	$3,609.14
Expenditures—June 23, 1933, to August 31, 1933	2,512.30
Balance	$1,096.84

BANK BALANCE

General Fund	$7,265.04
Research Fund	1,096.84
	$8,361.88
First National Bank, Checking Account	$1,985.68
First National Bank, Savings Account	$6,376.20
	$8,361.88

The following were elected to membership as of thirty days after the publication of their names provided no objections to any are received by the Secretary:

Active

Clark, John W.—Franklinville, N. C. Manager, Randolph Mills, Inc.

Gosman, Clarence R.—601 W. Harrison St., Monticello, Ind. Dyer, Thread Mills Co.

Kiviat, Frank—242 Washington Ave., Belleville, N. J. Technical Representative, The Hart Products Co., 1440 Broadway, New York, N. Y.

Klipstein, Herbert C.—34 Highland Ave., Montclair, N. J. Plant Manager, American Cyanamid & Chemical Co., Woodbridge, N. J.

Leaver, Harry—7 Highland Ave., Newport, N. H. Dyer, Gordon Woolen Co.

McCann, T. Arthur—399 Bank St., Fall River, Mass. Overseer of Dyeing, Algonquin Printing Co., 397 Bay St.

McClay, O. H.—27 Federal St., Springfield, Mass. Dyer, Farr Alpaca Co., Holyoke, Mass.

Young, Albert A.—4238 St. Paul Blvd., Rochester, N. Y. Foreman Chemist, Eastman Kodak Co., Kodak Park.

Zeuren, William—32 Union St., Shelton, Conn. Dyer.

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AMERICAN
DYESTUFF
REPORTER

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DECLINE

ACCORDING to figures of the Federal Reserve Board a decline in industrial activity has been apparent for the past two months. The report of the Board indicates that this decline has occurred chiefly in those industries in which expansion had been very rapid and was also quite marked in those industries in which processing taxes or codes had recently become effective.

General Johnson, Administrator of the NRA, dislikes the reference made to codes and has objected to it, the research director of the Reserve Board replying that such references were inadvertent. Whatever may be the cause of the decline, according to the figures reported by the Reserve Board it has taken place. On the other hand General Johnson reports that major industries with the exception of steel report a definite upward trend.

This contradiction may be explained away by the fact that apparently General Johnson may have in mind a more recent period than that covered by the Reserve Board report. The index of industrial production as determined by the Board and adjusted for seasonal trends was 60 last March. It then advanced to 100 in July and declined to 92 in August. A preliminary estimate for September places the index for that month at 84 and no estimate has been made for October. However, the weekly survey of business published by the Department of Commerce continues to show a decline. However, General Johnson's report, although not supported by government figures is significant in that it is the first to state with *assurance* that there is a definite upward trend.

Taking it for granted that the government figures are correct and General Johnson's report too optimistic, undue alarm need not be experienced over the decline. Such a decline is not without precedence. An alternation of gains and losses has been evident in the periods of recovery following other depressions. This fact was true in 1921 when the production index of the Federal Reserve Board reached a low of 64 in March and six months later it had advanced to 68.

The record of net gain for 1933 is more than six times as large for the same period in 1921 even after allowance for losses in August and September is made. We should not lose sight of this fact in spite of the assertion made by Mr. Hearst that NRA stands for "No Recovery Allowed." Let's wait a while before we definitely pass judgment on the NRA.

HIGHER PRICES

YOU may disagree completely with the purpose of the rather indefinite announcement of monetary policy made by President Roosevelt in his radio address to the nation recently. You may feel that the policy as thus far stated lacks soundness—and you'll have lots of company. You may feel that experimentation with the currency system of the type indicated will be eventually harmful; that the NRA to date has been a failure rather than a success; ditto for the AAA; that all this tinkering with "natural" economic laws can lead only to complete chaos sometime in the future. You may be convinced of all of these things, yet you cannot for a minute doubt the intention and the ability of the President to raise commodity prices.

He has restated as a definite policy his determination to raise the average of commodity prices to approximately the 1926 level, and then to stabilize them at that point through a managed currency probably involving adoption of the "commodity dollar." No one has to be an economic expert to know that the prices of commodities in which he is particularly interested have still a long way to go before they reach the 1926 level. The average advance necessary from present levels is estimated at about 45 per cent. No one has to be an economic genius to realize that the present Administration has the power to accomplish this end. The head of that Administration has stated that he will accomplish it, in one way or another.

Regardless of what may come after, it is positively assured that substantially higher prices are coming. They are coming inevitably in all raw materials and in all finished merchandise. How quickly they will materialize is anybody's guess, but the time for guessing as to the general price trend over the next few years is definitely over.

Presentation of Medal

The new Chemical Industry Medal of the American Section of the Society of Chemical Industry was presented on November 3rd to Mr. James G. Vail of the Philadelphia Quartz Co. at a meeting held at the Chemists' Club, New York City. The meeting was held jointly with the American Chemical Society, the Electro-chemical Society and the Societe de Chimie Industrielle.

S.O.C.M.A. Meeting

The regular monthly meeting and luncheon of the Synthetic Organic Chemical Manufacturers Association was held on October 19th at the Chemists' Club, New York City, with President Merz presiding.

It was reported to the meeting that as a result of the Government's economy program and the drastic curtailment of personnel, the Department of Commerce had decided to abandon certain statistical services, among them Bulletin No. 2865, covering the monthly imports of coal-tar dyes, synthetic aromatics, medicinals, intermediates and other products imported under paragraphs 27 and 28 of the 1930 Tariff Act. After earnest representations had been made of its vital importance to the industry and the latter's willingness to pay for the service, the Association was able to secure its retention.

It was reported by President Merz that at that time nothing more concerning the status of the Chemical Alliance Code was known and that the delay in progress toward final approval could not be attributed to the Alliance inasmuch as the NRA had held the code under consideration since Sept. 14th and the Code Committee of the Alliance was not called to Washington for a conference until October 19th. It was further reported that as yet no supplemental codes of the various sub-divisions of the industry had been filed but that there were a number in process of preparation and revision.

J. G. Lerch spoke at length on the possibilities of Section 3 (e) of the Recovery Act which provides for control of imports conflicting with the NRA and also gave a complete explanation of the benefits, as he saw them, to be derived from the recent decision on the dye-mixture case. For the first time in any decision the burden of proving all the elements of U. S. value was placed upon the importer; previously he had only to state in court that he knew of no competitive product and the government had to prove him wrong.

If suitable arrangements can be made, it was agreed that the annual meeting be held on Friday, December 8th, preferably at the Chemists' Club.

Opens New Office

The American Cyanamid & Chemical Corporation has opened an office in the New Center Building, Detroit, Michigan. The telephone number of the office is TRinity 2-1330. Mr. George S. Horsfull, who is the resident representative of the company, will be in charge of the new office.

Concerning Sodium Metasilicate

Sodium metasilicate, while known to science for nearly a century, has only within recent times been available in a satisfactory free flowing form. The material was introduced by the Philadelphia Quartz Company, of Philadelphia, as Metso and is covered by U. S. Pat. 1898707. It is a definite compound, having the chemical formula $Na_2SiO_3.5H_2O$.

The laundry industry was the first to use sodium metasilicate, as a soap builder. The outstanding improvement said be noted was the whiter appearance of white fabrics and the brightness of colors. It was logical therefore to consider metasilicate in conjunction with the various textile cleaning and washing processes.

As a kier assistant metasilicate was tried with good effect. It has been found that the "resists" in dyeing are greatly reduced. Some other properties of metasilicate said to be of special benefit are its quick wetting ability, its greater safety with fabrics, its free rinsing characteristic.

New du Pont Vat Paste

Leucosol Yellow K Paste (Patented), a vat color of the anthraquinone series prepared particularly for the printing trade, has just been announced by the Dyestuffs Division of E. I. du Pont de Nemours & Company. It is a non-drying paste; and, as it is being manufactured especially for printing purposes, it is claimed to be grit-free, non-foaming, and does not yield specky prints, settle out, or form crusts in the barrel.

Leucosol Yellow K Paste is said to be fast to light, soaping and commercial laundering, and is applicable to cotton, silk or rayon which is to be used for dress goods, draperies and similar materials.

Glyco Sales Representative

William A. Kingman, formerly chief chemist for the Dennison Manufacturing Company and later chemist for the Lowe Paper Company, has established headquarters at Framingham, Mass., Telephone 3476. He will act as a special sales representative for the Glyco Products Co., Inc., servicing their special water-soluble waxes, resins, solvents, emulsifying agents, etc.

Perkin Medal Award

Dr. Colin G. Fink, Professor of Electrochemistry at Columbia University, has been elected to receive the Perkin Medal of the Society of Chemical Industry for 1934. The medal is awarded annually for valuable work in applied chemistry and will be presented this year to Dr. Fink for his inventions in the fields of metallurgy and electrochemistry. The selection is made by a committee representative of five of the national chemical societies.

Presentation of the medal will be made at a meeting in New York early in January, details of which will be announced later.

The Significance of

Tensile Tests on Viscose Rayon*

By J. M. PRESTON

Producers and users carry out tensile tests on rayon yarns, but the meaning of these tests is imperfectly understood. The relations of the strengths and extensions to the structure, degradation, humidity, and other factors is discussed in this article and compared with those of other yarns. It is recommended to test rayon yarns both wet and dry and after a mild alkaline scour.

THE absolute value of the results obtained in any test of the tensile properties of rayon is dependent on the physical and chemical structure of the fibers of the rayon yarn. Thus the arrangement of the cellulose micelles in the fibers and the dimensions of the micelles (*i.e.*, the degree of degradation) determine what will be the tensile properties.

Micelle Structure of Fibers

When the micelles have the optimum arrangement for giving maximum strength they are oriented parallel to the fiber axis, and on being subjected to mechanical stress the micelles can only either extend, or break, or slip over one another. As the micelles are practically inextensible and as the force required to break the main valency chains of the micelles would be of the order of 800 kgs./mm., against the highest value actually found in any fiber of only about 100 kgs./mm., slippage of micelle on micelle must occur. This is confirmed by calculations made on the assumption of slippage, which gives values of the same order of magnitude as those of the best oriented cellulose fibers (Meyer and Mark, Der Aufbau der Hochpolymeren Organischen Naturstoffe, p. 152 *et seq;* Mark, Physik und Chemie der Cellulose, p. 161). Also such fibers are practically inextensible and crease badly, since any slight extension of one side of the fibers during bending is not subsequently recovered, as it is due to slippage. Lilienfeld viscose rayon, ramie and flax are more or less perfect examples of the class of fibers just considered. All other rayons than that just mentioned above have structures which differ to a more or less marked degree from a parallel arrangement of the micelles.

In general, viscose rayons have a better oriented layer on the outside or skin of the fiber (Preston, "J. Soc. Chem. Ind." *50,* 199-203 T. 1931; Van Bergen "Chemisch Weekblad," 30th year, 55-58, 1933) while the core has a more higgledy-piggledy arrangement. As Mark has pointed out, a transposition of the structures of the skin and the core would give a fiber with the optimum textile qualities, but this goal has not been attained except in small scale experiments, though Harrison (E.P. 351,527) has described a process which claims to produce fibers with this kind of structure. Since different layers of viscose rayon fibers have different structures, extension results in slippage in the well oriented outer layer simultaneously with a rotation and parallelization of the inner higgledy-piggledy layers, till eventually a stage is reached at which no more parallelization is possible and the fiber breaks on further extension.

Viscose rayon fibers, when extended beyond a certain stage, do not recover their original length when the stress is removed; the possibility of any recovery seems to be due to strains in the micellar structure which have not been entirely destroyed by slippage between the micelles. The ability of the viscose rayon fibers to extend is thus seen to be a consequence of their peculiar structure. The more parallel the arrangement, the less the extensibility; the greater the strength and the less the resistance to creasing. The degree of parallelization of the micelles in the fiber can be determined by X-ray spectroscopy (cf. Clark and Corrigan, "J. Ind. and Eng. Chem." *22,* 474-487, 1930), or by measurements of the refractive indices of the fibers (Preston, "Trans. Far. Soc." *29,* 65-71, 1933) and the tensile properties deduced from the micellar theory of fiber structure and the measurements made by these methods are in agreement with the directly measured tensile properties.

Cellulose Degradation

With fibers of identical structural type, the only other intrinsic factor is the degree of degradation of the cellulose, and the only important extrinsic factors are the moisture content and the twist. The degree of degradation as measured by the fluidity of cuprammonium solutions of

*The Textile Manufacturer.

the fibers is directly related to the strength of the fibers (Ridge and Bowden, "J. Text. Inst." *23,* T. 319-366, 1932) on the one hand, and to the length of the micelles on the other hand as shown by Staudinger ("Trans. Far. Soc.," *29,* 18-32, 1933). Consequently the strength of a cellulose fiber is seen to be controlled by two important factors: the length of the micelles (*i.e.,* the degree of degradation); the arrangement of the micelles.

The degree of degradation is shown more clearly in the tensile properties of the yarn when the yarn has received an alkaline scour. Even good quality yarns, as received from the manufacturers, lose a few per cent of strength after a mild alkaline scour, but severely degraded yarns, though already weakened, may lose a further 50% of their strength. Thus damage due to degradation of a chemical character is evaluated best by making tensile tests both before and after a mild alkaline scour. For this purpose Whittaker ("J. Soc. Dyer and Col." *49,* 9-19, 1933), recommends scouring for half-an-hour at 40° C. in 0.5% soap solution. The loss in strength produced by the scour in degraded yarns is most marked in their wet strengths, and in addition there is a marked fall in their extensibility.

Effect of Humidity

The effect of the humidity of the atmosphere surrounding the yarn is important as it controls the moisture content of the yarn, which in turn exerts a big effect on the tensile properties of the yarn. Cotton (Mann, "J. Text. Inst." *18,* 253 T, 1927) and flax fibers and cotton yarns (Pierce and Stephenson, "J. Text. Inst." *17,* T. 645, 1926) show greater strengths at high humidities than at low, though the magnitude of the effect is only small. An increase in strength occurs of about 10% between relative humidities of 40% and 100%. On the other hand, with cellulose rayons the magnitude of the effect is large and in the contrary direction. For viscose and cuprammonium rayons there is a loss of strength of 60-70% when the relative humidity is increased from 40% to 100% (Herzog-Wagner, "Faserstoff-Praktikum," p. 114; King and Johnson, "J. Soc. Dyer and Col." *44,* 346, 1928). The magnitude of the strength loss is not quite so great in the case of Lilienfeld viscose and cellulose acetate rayons. The loss of strength of cellulose rayons with increasing humidity is a function of the degree of degradation of the cellulose. Thus, from the data of Ridge and Bowden (*loc. cit*), there is increasingly greater loss of strength on wetting rayon, the greater its fluidity. As far as the loss of strength with increased humidity is concerned, the rayons behave similarly to real silk, in which also there is considerable loss of strength (Denham and Lonsdale, "Trans. Far. Soc.," *29,* 305-316, 1933), about 20% loss occurring between 40% and 100% relative humidities.

Extensibility of Rayon Yarns

The extensibility of cotton yarns (Pierce and Stephenson, *loc. cit.*), increases with increasing humidity, an increase of over 100% occurring between 40% and 100% relative humidities; similarly with real silk (Denham and Lonsdale, *loc. cit.*), the extensibility is nearly doubled when the relative humidity is increased from 40% to 100%. With cellulose rayons the effect of humidity on the extensibility is complicated by other factors: sometimes the extensibility of the wet yarn is greater than that of the dry and at other times the contrary is the case. In general it can be stated that the wet extensibility is greater than the dry when the cellulose of the rayon is not much degraded, but when the cellulose has been degraded to a greater degree (fluidity $>$ 15, say), the dry extensibility is greater than the wet. From the foregoing it is obvious that it is impossible to state what will be the effect of humidity on the extensibility of a rayon unless other factors are known, of which the principal one is the degree of degradation of the cellulose. The effect of the degree of degradation on the wet extensibility of rayon yarns is very important when the utilization of these in fabrics is considered. For example, in a warp-knitted fabric the low wet extensibility due to degradation of but one thread is enough to ruin a whole piece of fabric since the inability of this thread to extend under localized strains can result in that one degraded thread breaking from one end of the piece to the other. In woven fabrics, the harmful effect of an exceptionally degraded thread is less important, since it will only cause damage over a short length of the fabric if it is in the weft.

The effect of degradation in lowering the tensile qualities of rayon is much increased when the rayon is submitted to a mild alkaline scour, as stated earlier. This is most important as it means that the low quality of a yarn may be discovered only after it is made up into fabric and has reached the stage of wet processing. Therefore it is an advantage, when fluidity measurements are not made, to test yarns not only wet and dry, but also after receiving a mild alkaline scour.

Standards in Testing

The B.I.S.F.A. rules for the testing and standardization of rayons lay down the limits within which denier may vary, and the conditions of twist, humidity and temperature under which tensile tests should be carried out, but no specification is given of the limits within which the values of tensile tests should lie. In this respect B.I.S.F.A. is not exceptional for there are no accepted standards available. As far as tensile strengths and elongations are concerned the values for commercial yarns given by King and Johnson (*loc. cit.*), and the degree of degradation of the cellulose in normal commercial yarns given by Ridge, Parsons and Corner ("J. Text. Inst." *22,* T. 117, 1931), are useful guides by which a yarn may be judged. But these data can be no more than this since makers do not guarantee their yarns to have given values. Generally

(Continued on page 681)

Sources of Some Faults in

Woolen, Worsted or Knitted Fabrics*

By L. L. LLOYD

Bradford Technical College

STANDARDIZATION of processes from raw material to finished fabric is essential for the production of fabrics that are practically free of faults. In standardizing processes team-work is necessary, and only in this manner is it possible to obtain superior results of one even nature for each type of fabric produced.

Failure in the selection of uniform materials may lead to irregularities where two different fibers are blended together before spinning. Not only the same weights must be blended, but also the two materials should have as near as possible the same staple lengths. In a union of viscose and wool two runs were used, in one of which the viscose was shorter in length and consequently worked more on to the face of the fabric during finishing, the result giving a barry effect.

Any deviation from the accepted method of dealing with any definite fabric may lead to trouble in a succeeding operation. It should be the duty of workpeople to notify the head of the department of any irregularities that are observed, as in this manner faults may be prevented or the number reduced. As an example a standard make of worsted cloth was produced on a loom in which the mails were rusted. The rust was collected by the oil present on the warp and crabbing fixed the oil so that it was not removed by normal scouring. The piece when finished had many dark lines warpwise, and these on analysis were found to contain more iron than the remainder of the yarn, the amount varied in different parts of the yarn throughout the run of the fabric. By analysis it was impossible to state whether the oil that had been employed was a genuine olive oil, but it most probably contained some tea seed oil, as this oil is one that readily polymerizes, and it has been found that iron promotes the polymerization by heat, even crabbing is sufficient to produce this change. If the scourer had been notified that rust was present on the loom a solvent scouring method could have been used that would have eliminated the fault. Goods that are modified in this manner cannot be finished satisfactorily compared with unaffected material, if they are processed by the normal method and are then cobbled to attempt to correct them. There are many commission dyers who treat all materials with solvent scouring agents because this overcomes many difficulties that are caused by the employment of unsuitable oils for the spinning operation.

Carbonizing and Dyeing

Scouring and milling are sources of many faults, but with woolens carbonizing is the root of many defects. The uneven distribution of sulfuric acid is one of the chief causes of color defects, and another is that of uneven heat treatment during the baking of the acidified material. There is no doubt that open width squeezing is the best method, but this should be followed by slow evaporation of the moisture before heating to the desired carbonizing temperature. Squeezing in rope form, followed by open width squeezing, is the best method for obtaining even acid content in the materials before drying and baking. A varying acid content will modify the dyeing properties of the wool. Again many dyers have the idea that the use of large quantities of Glauber's salt will give level dyeing no matter what percentage of acid is in the goods; such dyers do not rinse the goods well enough to lower the acid content and obtain a uniform acid distribution. Many woolens dyed under these conditions show a skittery appearance which in most cases may be prevented if the goods are well rinsed in the winch machine and then boiled with as short a bath as possible along with a neutral foaming agent. The bath may then be cooled by addition of water and the dyeing operated in this bath. The foaming agents will aid level dyeing and also aid in the production of a soft handle. The new Spooner Carbonizing Plant, in which the material is carbonized without the use of a tentering system, has many advantages over other machines, and is applicable to all varieties of wool goods.

Tinting for Sighting

The use of highly-twisted yarns has greatly increased the necessity of sighting of these yarns for weaving, and

* Abstract of Paper read to The Textile Institute Conference at Harrogate. Reprinted from *The Textile Manufacturer.*

many defects, particularly with regard to color, are due to the nature of the sighting color. Soluble Blue and Magenta are largely used for this purpose. These colors are apparently discharged during the scouring operation. They are, however, not removed but are so greatly reduced in intensity that they appear free of color, but when the goods are treated in an acid bath the color returns. This occurs during the dyeing operation, often with unpleasant results because the tinting of the twist yarns is not even and the color also affects the shade of the dyed materials. Insoluble colored compounds are favored by many spinners, particularly of yellow ochre and of ultramarine. With many highly twisted yarns it is almost impossible thoroughly to remove these substances during the scouring operation, with the result that the shade of the final product is impaired. These substances are often used to color a top very heavily indeed, some of this top being then blended with white wool for the production of tinted yarns. Insoluble colored substances do not combine with the wool and consequently, during processing, there is always the possibility of these agents contaminating the atmosphere of the spinning and weaving sheds. They may constitute a danger to the health of the operatives. There are many dyestuffs used for tinting purposes that are satisfactory for the sighting of woolen and worsted yarns, provided that the material has not to be submitted to a high temperature wet process, crabbing being probably the most damaging treatment because it fixes the color. These colors are removed from the material after crabbing by any acid process that follows, such as in dyeing; they are removed to a very great extent by scouring and do not color any other yarns, with the possible exception of cellulose acetate rayon. As these colors are mainly used for tinting crepe yarns, they will be removed in the acid bath in which the material is creped. Indigocarmine has been used for a long time as tinting agent and is satisfactory provided that the color is removed before any heat treatment is applied. Many direct cotton colors have also been used, but with these again there is the difficulty of complete removal. With such tints removal with hydrosulfite is usually employed for complete removal, a process which increases the cost of finishing, and also modifies the finish of the goods.

In testing, tinted yarn should be submitted to every possible operation to which it may be submitted before testing to find whether it is removed by scouring.

Wax Rods and Acetate Silk

Paraffin wax rods as an aid to weaving may be of great assistance to the manufacturer but they are a great hindrance to the dyer and finisher. Defects produced by wax are mainly present in goods produced from cellulose acetate rayon warps, although other fabrics also suffer. The trouble with goods containing cellulose acetate rayon is that they cannot be rigorously scoured by alkaline scouring agents on account of the effect of hydrolysis of this compound. The hydrolysis of the cellulose acetate rayon modifies the dyeing properties such that direct cotton colors will then heavily color the fiber. Paraffin wax is more easily removed by the employment of solvent scouring agents but most of these affect cellulose acetate rayon. The wax will dissolve dyestuffs that are used for the dyeing of cellulose acetate, and as the paraffin generally collects as globules between the interstices of warp and weft they become very prominent after finishing. Emulsifiable wax rods are now available; they are more expensive than paraffin wax, but their use would be an economic one. The new rods are slightly dark in color but they do not transfer any color to any textile fiber after removal by the scouring operation. The presence of paraffin wax on textile materials, when it is unevenly distributed, has the effect of modifying the shade by altering the light reflecting properties. A dull warp streakiness may be caused by hot pressing, which slightly diffuses the wax into neighboring threads.

Knitted Goods Faults

In the knitting industry many color defects are produced through carelessness. It is perhaps as necessary to work up separate runs of yarn of the same shade and dimensions as is necessary in the woven goods trade. Variation of the moisture content (condition) of all types of yarns leads to a large variety of defects. It affects the subsequent shrinkage during finishing as tension readily affects over-conditioned yarn. Again tension is of very great importance especially when the goods have to be piece dyed. On account of shrinkage many knit goods are rapidly scoured and consequently are poorly washed, with the result that insoluble soaps are often left on the goods. These not only affect the color but are also a source of bad odor which gradually develops when the goods are stored. This fault is also common with scoured dyed yarn for the knit goods trade. The use of the neutral foaming agents applied from an acid bath are of great value for the removal of insoluble soaps and they also improve the handle of the goods produced.

Cleanliness of machinery is as necessary with knitting machines as it is with looms. Rusty needles are a source of rust stains which cause many troubles during dyeing and finishing. One of the most serious defects is that due to rust stains when the goods have to be peroxide bleached. The rust acts as a catalyst causing rapid decomposition of the peroxide such that the rust stains cause local excessive action with the result that the wool is decomposed, usually with the formation of holes where the rust stains were. This, of course, cannot be detected in the finished material and one has to surmise that it was caused by either copper or iron stains. If rust or copper stains are observed after scouring they should be removed before bleaching; the rust stains by means of oxalic acid, preferably followed by treatment with a neutral foaming agent, and the copper by a cold solution of cyanide followed by well rinsing. If the material has to be dyed the satins should

also be removed because they affect the shade of so many dyestuffs.

Another blemish is that due to the use of jute packs that have been produced from dyed jute. The usual color of dyed jute for this purpose is a deep blue produced by means of a basic dyestuff. Very small amounts of this dyed jute get into the raw wool and cause contamination of the whole batch of wool. The jute is partly removed during carding but much of it is powdered or broken into very small fragments which adhere to the wool. If the jute were undyed it would not cause a blemish in white goods, but the colored jute is a source of small stains that impair the value of goods produced from such material. The jute is broken by the Harmel crusher into extremely small fragments which cause the blemish by color bleeding during finishing; the color bleeding mainly taking place when the goods are sulfur dioxide bleached or stoved. This trouble is a serious one because tops for this class of trade are produced without tinting; yet color defects may develop that would be too costly to remove.

Oil stains are very common in knit goods. If the goods were scoured with the aid of a solvent scouring agent, the majority of these defects would be prevented. A much safer method would be that of using a blended emulsifiable oil for lubrication.

TENSILE TESTS ON VISCOSE RAYON

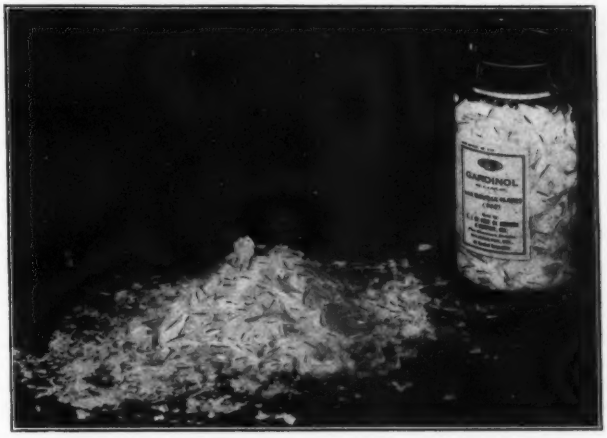
(Continued from page 678)

the yarns are sold on the understanding that they shall be of good tensile quality and capable of being formed into satisfactory fabrics. Thus, except in extreme cases, quantitative values are only useful in providing a basis for a personal opinion. One yarn may be said to have better qualities than another, but this does not prove that the inferior one is not of good quality or is not usable, although, if it can be shown that certain yarns in a delivery are much inferior to the average and if these yarns give trouble in processing, then the relative quantitative values of the tensile tests are valuable evidence.

The twist has an important bearing on the strength of staple fiber yarns, since the binding together of the individual fibers is dependent entirely on the twist. In a singles cotton yarn the strength increases with the twist up to a maximum at a twist constant (multiplied by square root of cotton counts) of about 5, and thereafter diminishes again with still higher twists. The importance of the interlocking effect of the twist on the fibers in a staple yarn is also seen from the results of Clegg ("J. Text. Inst." *17*, T. 591, 1926), who found that the strength of a cotton yarn is only about 50% of the sum of the strengths of the constituent fibers and that about 50% only of the hairs break, the remainder slipping. In staple fiber rayon yarns, a similar optimum twist must occur, but with normal continuous filament yarns twists up to 20 turns per in. have no effect on the strength or extensibility. At higher twists both the strength and extensibility diminish, the strength falling to about 50% at 50 turns per in. and the extensibility falling by about 20% (Hamm and Cleveland, Bur. of Stand. "J. of Res." *7*, 617, 1931).

New Gardinol Development

The Gardinol Corporation announces a new development in the manufacture of their Gardinol products. These products are now being offered to the trade in flake form



and sold under the name of Gardinol WA Double Flakes and Gardinol CA Flakes. Both of these products are being manufactured in this country and offer the advantage of being non-dusting. The new flakes are also said to be very easily dispersed and readily soluble in warm water besides offering all the superior properties of the older powder types.

Azo Dyestuffs

German Patent No. 468,200 (25/X/'28) (*addition to G. P. No.* 446,495 *of* 8/XI/'24)—*I. G. Farben-Ind. A.-G.*—The original patent covers the reduction, with alkaline reducing agents, of azo dyestuffs from sulfonated p-nitro-amines or their derivatives, and suitable second components, in such a way that every two mols. are condensed (the conditions must be such that the azo linkages are not interferred with, but that the nitro-groups, by pairs, are condensed to an azoxy or azo group). The present addition permits the original azo dyestuffs to contain no sulfonic groups, these being introduced after reduction, or, alternatively, before reduction. Of two examples given, one involves the coupling of diazotized p-nitroaniline to salicylic acid, the product being reduced in alkaline reaction (caustic and zincdust, e.g.) and the reduction product sulfonated with oleum of 23% at 100° C. The products, salted out finally as Na salts, dye animal or vegetable fibers a brown-orange.

Tube-Tex Machine

A new machine that is said to extract, process, dry, finish, condition and measure tubular knit goods, all in one continuous operation, is now being made by H. W. Butterworth & Sons Co., of Philadelphia. Only two operators are required on this machine—a third being required for sorting and sewing. This machine is known as the "Tube-Tex." It is claimed that from 2,800 to 3,000 pounds of fabric can be processed and finished in eight hours.

The advantages claimed for the machine are: That it saves 10-25% in horse power—50-75% floor space—considerable steam and reduces labor costs from 50 to 75%, any reasonable desired regain can be obtained and losses at the end of the rolls are never more than three inches. The quality of the fabric is said to be improved and there is a uniformity of face and width. The yield is controlled and all moire is eliminated.

In the processing operation the fabric, preparatory to passing through the machine, may be weighed or dried in rope or flat form. It passes through the machine in continuous endless length at the rate of from 25 to 35 yards per minute. The fabric can be taken directly from a dye beck and passes through pot eye guides. Afterwards, it is opened up fully by a driven spreader which consists of two upper and two lower horizontal rollers and also two smaller vertical rollers on each side.

One each of the upper and lower rollers is driven, the two side rollers are driven by spur gears. By regulating the speed of these rolls the fabric can be stretched or allowed to run full. The fabric, after it is stretched to its full dimension by the driven spreader, is passed under the immersion roll, and then through squeeze rolls. If finish is required, the liquid for de-lustering, sizing, stiffening, etc., may be poured over the goods at the top of the squeeze rolls, squeezed, and then allowed to run down to the immersion pans, from which its is re-circulated.

From this machine the goods pass into the drier, which is made of asbestos-lined sheet metal. The house is 20 ft. long, 36 inches wide, and has five horizontal air passages. The bottom passage holds four layers of fabric, and the other passages three layers each. The fabric is carried through the drier, free from tension at all times, except where tension is applied by spreader units. There is a mechanism which insures uniformity; tension being applied to the fabric as it emerges from the drier, and before it passes to the final finishing machine. The heat from the drier is exhausted from the top, and drawn in at the bottom. From the drier the goods enter the finishing machine.

Here the fabric is streamed from top and bottom, and opened up by the driven spreader. It is steamed again, and passes through the finishing rolls. Before being wound up it is cooled by a process which insures the proper amount of moisture being left in the fabric.

The driving of the entire machine is done by DC motors, of which there are three. An AC-DC motor generator set is part of the equipment of each machine. A separate hand control governs the speed of all three motors at one time, insuring perfect synchronization. There is a feeder control between the various units of the entire machine.

Operation is by push button control at each end. The machine is also equipped with signal lights, and has a semi-automatic arrangement which slows the machine when cutting and doffing is being done.

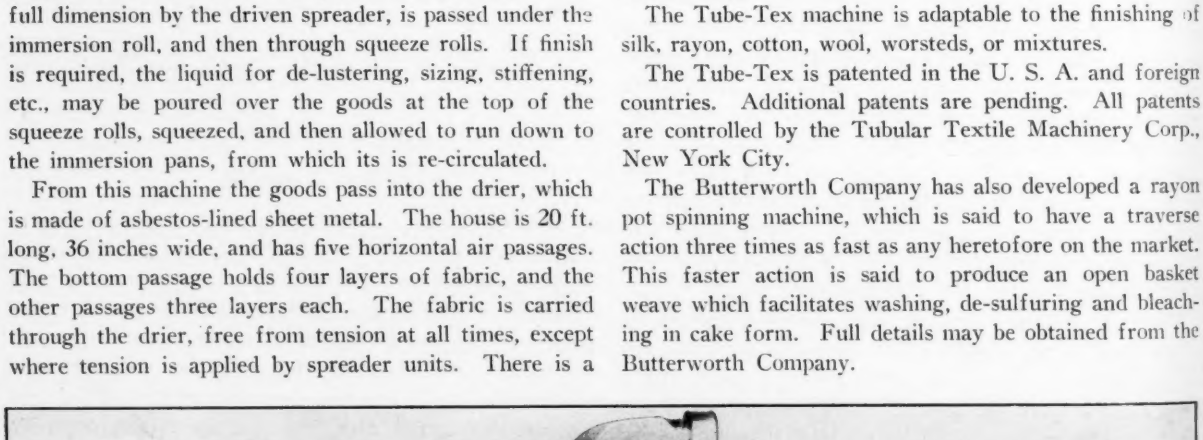
The separate units of this machine can be supplied. A single unit at the beginning of the machine can be used for processing after the goods have been centrifuged. A second unit, similar to the first, except that it has an extra set of squeeze rolls, permits the goods being taken directly from the dye beck kettle.

It is claimed for the machine that the goods can be taken from the dye kettle, and finished in roll form in five minutes.

The Tube-Tex machine is adaptable to the finishing of silk, rayon, cotton, wool, worsteds, or mixtures.

The Tube-Tex is patented in the U. S. A. and foreign countries. Additional patents are pending. All patents are controlled by the Tubular Textile Machinery Corp., New York City.

The Butterworth Company has also developed a rayon pot spinning machine, which is said to have a traverse action three times as fast as any heretofore on the market. This faster action is said to produce an open basket weave which facilitates washing, de-sulfuring and bleaching in cake form. Full details may be obtained from the Butterworth Company.



Butterworth Tube-Tex Machine.

BOOK REVIEWS

A. S. T. M. Standards on Textile Materials—*By Committee D-13 of the A. S. T. M., 164 pages, $1.00 per copy from the A. S. T. M. headquarters, 1315 Spruce St., Philadelphia, Pa.*

This publication contains all of the 30 standard and tentative specifications, methods of testing and definitions pertaining to textile materials, which have been issued by the American Society for Testing Materials, through the work of its Committee D-13 on Textile Materials. This is the first compilation of A. S. T. M. standards covering these materials since 1930. Many new standards have been issued since the appearance of the earlier publication so the present edition should be of much convenience to those dealing with textile materials.

New tentative standards just issued this year cover Holland cloth, asbestos roving and tests for small amounts of copper and manganese in textiles.

Several of the specifications and test methods previously issued as tentative were adopted as standard this year. They include tolerances and tests for knit goods, specifications and tests for Cuban (jute) raw sugar bags and for asbestos tape for electrical purposes, and specifications for chafer tire fabrics and enameling duck for the tire industry.

Specifications for a number of materials were revised this year. The latest revisions (either adopted or to be tentative for a year) are given. They cover tire fabrics (other than cord), tire cord (woven and on cones), hose ducks and belt ducks, cotton yarn (single and plied), electrical cotton yarns, cotton sewing threads and light and medium weight cotton fabrics. Proposed revisions in the standard methods of testing woven textile fabrics are detailed. Revisions (issued previous to this year) in the specifications for textile testing machines and for asbestos yarns were adopted this year and are given in the book.

In addition to the materials listed above, there are a number of others covered by standards or tentative standards approved prior to this year, including numbered cotton duck, Osnaburg cement sacks, goods for rubber and pyroxylin coating, tubular sleeving and braids, silk and cotton tapes, 0.007-in. cotton electrical tapes, and rayon; also methods of determining the scoured content of grease wool and allied fibers and determination of relative humidity.

In addition to the standards, the book includes a psychrometric relative humidity table which combines accuracy and convenience; photomicrographs of common textile fibers; and a proposed potassium dichromate oxidation method for the determination of total iron in asbestos textiles.

Chemical Economics—*By Williams Haynes. D. Van Nostrand & Company, New York. 300 pages. $3.25 per copy.*

In this volume Mr. Haynes, publisher of *Chemical Markets*, has brought together a mass of information for the student of chemical economics. In the words of the author the purpose of the book is to set forth clearly the economic principles that underlie the making and selling of chemicals and also to endeavor to show the part played by chemicals in the development of modern industrialism and to place the chemical industry in its proper relationships within our economic industry. This book fills a proper place in the economic and chemical world inasmuch as the chemical industry has been neglected by professional economists probably because of its highly technical character and also because chemical statistics are not as complete as in many other industries.

The book is divided into two parts; part one being entitled "Economic Foundations of the Chemical Industry" and part two entitled "Historical Background of the Chemical Industry." To give the reader a general idea of what the book contains we will list the chapter headings herewith: Part One—Introduction; Chapter I—Chemicals in Industry; Chapter II—Chemical Production; Chapter III—Chemical Supply and Demand; Chapter IV—Cost, Value and Price; Chapter V—Chemical Distribution. Part Two—Chapter VI—Industrial Evolution; Chapter VII—American Chemical Backgrounds; Chapter VIII—American Chemical Industries; Chapter IX—World War and Chemical Industry; Chapter X—Cartels and Consolidations; Chapter XI—American Chemical Mergers; Chapter XII—The Chemical Future. The book is adequately illustrated with graphs, portraits and other half-tones.

To the chemist whose education or experience has been largely limited to the technical applications of his art or to the economist whose knowledge of technical chemical operations is somewhat vague we heartily recommend Mr. Haynes' new book.

Offers New Associate Membership

For the purpose of bringing younger chemists and chemical engineers interested in industrial chemistry into touch with the work of the Society, a new form of Associate Membership has been established by the Society of Chemical Industry, which is very similar to the Junior Membership in other societies.

To be eligible for Associate Membership, the applicant must be under 23 years of age. His Associate Membership automatically terminates the end of the year in which he reaches 23 years of age.

The subscription for Associate Members is 7 s. 6 d. ($1.90) per year, payable directly to the General Secretary in London or to the local section secretary.

Associate Members will not receive the weekly journal of the Society. They will receive the Annual Reports on the Progress of Applied Chemistry, a volume of some

700 pages covering 24 chapters, each written by an expert or a group of experts in his field. This volume is an annual summary of the progress of applied chemistry which is recognized as authoritative throughout the English speaking world. The normal price of that review is 12 s. 6 d. ($3.15), so that the value of that publication is in excess of the Associate Membership fee. Associate Members shall also have all the other privileges of Membership except the right to vote.

This form of Membership is particularly adapted to the chemical engineering student or to the recent graduate.

Membership applications can be obtained from the Honorary Local Secretary, Foster Dee Snell, 305 Washington Street, Brooklyn, N. Y.

TECHNICAL NOTES FROM FOREIGN SOURCES

"Color"

René Toussaint (*tr. Prof. O. Bizioli*)—*Tinctoria* 31, 515 (1932).—The second part of the paper. A general survey of the subject of dyeing, from the coloristic viewpoint, interestingly taken up. Some of the subjects dealt with in this section are—tolerance of difference between sample and dyeing (i.e., the limits of allowable discrepancy), ocular error within the visible limits of the spectrum, the correction of faulty dyeings, study of concentrations, of purity of tone, of luminosity, and of brilliance of tone.

Vat Dyestuffs (Benzanthrone Series)

German Patent No. 467,697 (11/X/'28)—*I. G. Farben-Ind. A.-G.*—The process patented consists in condensing benzanthrones, alkylated, arylated, or aralkylated in the bz-2 or bz-3 position, into dibenzanthrones or iso-dibenzanthrones, by the customary methods (fusion with caustic, etc.) For example, a mixture of 10 parts of bz-2-methylbenzanthrone and 12.5 parts of glucose are fused with KOH at 230°-240°. As soon as the lively evolution of gas is over, the reaction is complete. The product is isolated as usual from such caustic melts. The product is bz-2-bz-2'-dimethylbenzanthrone, and can be isolated in the pure state by extraction with organic solvents from the crude product. It dyes cotton a blue-violet from a blue vat. Dyeings from it do not appear redder when wet, as is the case with dibenzanthrones.

The methyl-benzanthrone cited may be produced by condensation of a-methyl-acrolein with anthrone.

Four examples are given.

Vat Dyestuffs (Anthraquinone Series)

German Patent No. 468,350 (1/XI/'28)—*I. G. Farben-Ind. A.-G.*—1-Aminoanthraquinone can be condensed with bz-1-halogenated benzanthrones to form benzanthronyl-1-amino-anthraquinones (G. P. No. 212,471), which are useful as dyestuffs. The present procedure oxidizes these products, and thus obtains dyestuffs quite different from the fundamental substances; valuable in themselves as dyestuffs, or as intermediates suitable for working up to other useful final products. In the example given, 10 part of bz-1-benzanthronyl-1-aminoanthraquinone, dissolved in 150 parts of conc. sulfuric acid, are oxidized at 0° C. with a suspension of 10 parts of artificial MnO_2 in 40 parts of sulfuric acid. This mixture is stirred until no further change of color takes place, upon which the whole is stirred into 1,000 parts of water, 10 parts of sodium bisulfite liquor added, and the whole boiled up and filtered. The product is a violet-blue precipitate; its vat is reddish-brown, cotton is dyed in it the same color, and the color after oxidation is a reddish blue.

The exact classification of the product, outside of its being a vat dyestuff, is doubtful, as one cannot say whether the benzanthrone nucleus or the anthraquinone nucleus is the fundamental grouping or the substituent one.

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